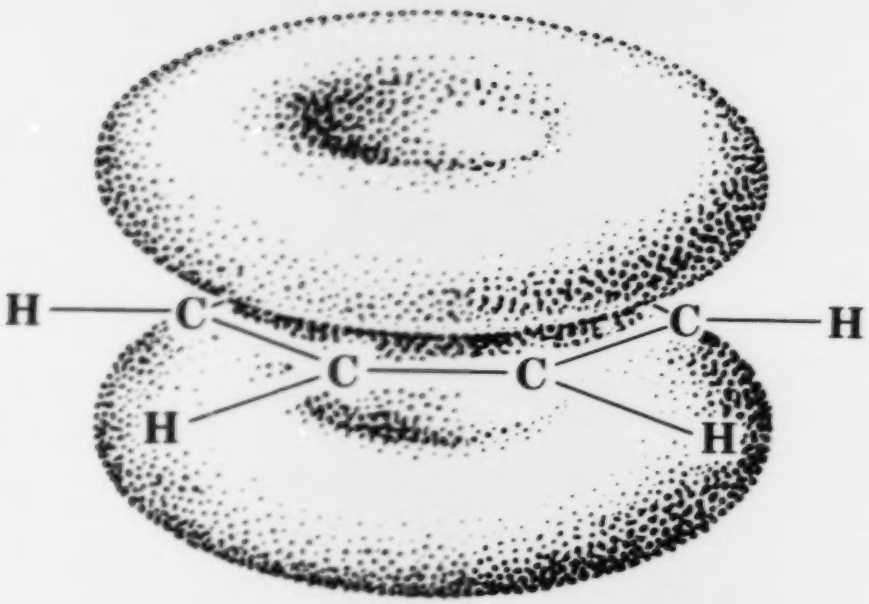
National Inventory of Sources and Emissions of Benzene (1985)

Report EPS 5/AP/1
March 1990



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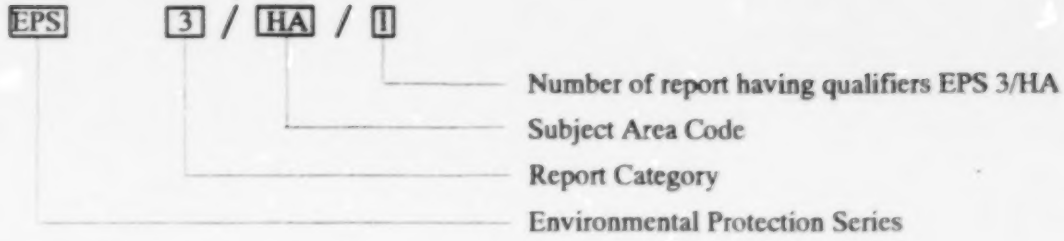

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NATIONAL INVENTORY OF SOURCES AND EMISSIONS OF BENZENE (1985)

by

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EPS 5/AP/1
March 1990

90-04606/

Canadian Cataloguing in Publication Data

Jaques, A. P

National inventory of sources and emissions of benzene (1985)

(Report ; EPS 5/AP/1)
Includes an abstract in French.
Includes bibliographical references.
Issued by Conservation and Protection.
ISBN 0-662-17591-3
DSS cat. no. En49-5/5-1E

1. Benzene -- Environmental aspects. 2. Pollution -- Measurement. 3. Benzene as fuel -- Environmental aspects. 4. Canada -- Industries -- Environmental aspects. I. Canada. Environment Canada. II. Canada. Conservation and Protection. III. Title. IV. Series: Report (Canada. Environment Canada) ; EPS 5/AP/1).

TD887.H93J63 1990 363.7'28 C90-098571-2

© Minister of Supply and Services Canada 1990
Catalogue No. En 49-5/5-1E
ISBN 0-662-17591-3
BEAUREGARD PRINTERS LIMITED

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ABSTRACT

Estimates of the quantities of benzene released to the environment as emissions in 1985 are summarized in this report. Emissions have been classified by source, sector, and province. The data presented are estimates based on sampling data, process emission factors, and production figures. Total anthropogenic emissions of benzene in 1985 were estimated at 34 150 tonnes, with transportation sources accounting for 76 % of the total.

A brief summary of the sources and uses of benzene has been included as well as a summary of the health effects of benzene. An analysis and description of trends in benzene emissions are also presented. The methods used to estimate emissions and the accuracy of the data recorded have been described.

RÉSUMÉ

L'objet du présent rapport est de résumer les estimations des émissions de benzène dans l'environnement en 1985. Les émissions ont été classées par source, secteur et province. On a effectué les calculs en se fondant sur des données d'échantillonnage, des facteurs d'émission établis pour les divers procédés examinés et des chiffres de production. En 1985, les émissions anthropiques totales de benzène ont été évaluées à 34 150 t, dont 76 % provenaient du secteur des transports.

Le document fournit un bref résumé des sources et utilisations du benzène et de ses effets sur la santé ainsi qu'une analyse et une description des tendances quant aux émissions de benzène. On y traite aussi des méthodes employées pour estimer les émissions et de l'exactitude des données publiées.

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SUMMARY

This inventory identifies anthropogenic sources of benzene released to the environment as emissions. For the purposes of this report, emissions have been defined as gaseous releases to the atmosphere.

Benzene emissions in Canada for 1985 have been estimated and are shown in Table S.1. Figures S.1 and S.2 provide a breakdown of emissions by province and source.

Total anthropogenic emissions of benzene in 1985 were estimated to be 34 150 tonnes. Combustion of gasoline and diesel fuels accounted for an estimated 25 895 tonnes (76 % of the total). Emissions from benzene and other chemical production were estimated to be 4 846 tonnes (14 %); stationary fuel combustion 1 405 tonnes (4 %); and gasoline marketing 654 tonnes (2 %) of the total emissions for 1985. The remaining 4 % were contributed by other miscellaneous and industrial sources.

Comparison of the data in this report with data for previous years indicates that emissions have been declining since 1980, mainly because of the decline in automobile emissions.

TABLE S.1 SUMMARY OF EMISSIONS OF BENZENE IN 1985 (tonnes)

Sector	Nfld.	P.E.I.	N.S.	N.B.	Que.	Ont.	Man.	Sask.	Alta.	B.C.	Terr.	Canada	% of Total
Industrial Processes:													
Crude Oil Operations			<1	<1	1	<1		7	52	3		64	0.19
Petroleum Refineries			31	18	60	55		26	51	61		302	0.88
Benzene Production					324	1604			292			2220	6.50
Chemical Production					160	1296			1141	27		2626	7.69
Primary Iron and Steel Production			10			313	17	<1		<1		343	1.00
Solvent Use	12	3	17	10	132	177	21	20	46	37	1	500	1.47
Fuel Combustion - Stationary Sources:													
Power Generation	<1	<1	<1	<1	<1	1	<1	1	1	<1	<1	4	0.01
Industrial Fuel Combustion	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	0.00
Commercial Fuel Combustion	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0.00
Residential Fuel Combustion	140	36	56	56	532	498	28	28	28	14	14	1400	4.10
Fuel Combustion - Transportation Sources:													
Light-duty Vehicles	365	109	766	646	3986	7268	1033	1090	2397	3120	58	20 818	60.96
Heavy-duty Vehicles	41	12	79	76	208	555	106	165	220	323	31	1814	5.31
Aircraft	5	1	3	8	52	93	10	16	48	40	15	288	0.84
Rail Transport	5	<1	2	1	10	17	10	6	19	10	<1	80	0.23
Marine Transport	29	<1	21	12	92	290	34	36	65	121	<1	700	2.05
Offroad Gas	27	6	26	30	89	265	150	382	625	136	14	1730	5.07
Other Diesel	9	2	16	8	54	83	24	67	113	77	12	465	1.36
Solid Waste Incineration:													
Municipal Refuse		4			63	63				4		116	0.34
Miscellaneous Sources:													
Gasoline Marketing	11	4	22	19	140	250	27	27	78	70	2	654	1.92
Benzene Loading Operations:					2	20			3			25	0.07
Totals	644	197	1049	887	3912	12 760	1480	1832	5179	4068	142	34 150	99.99

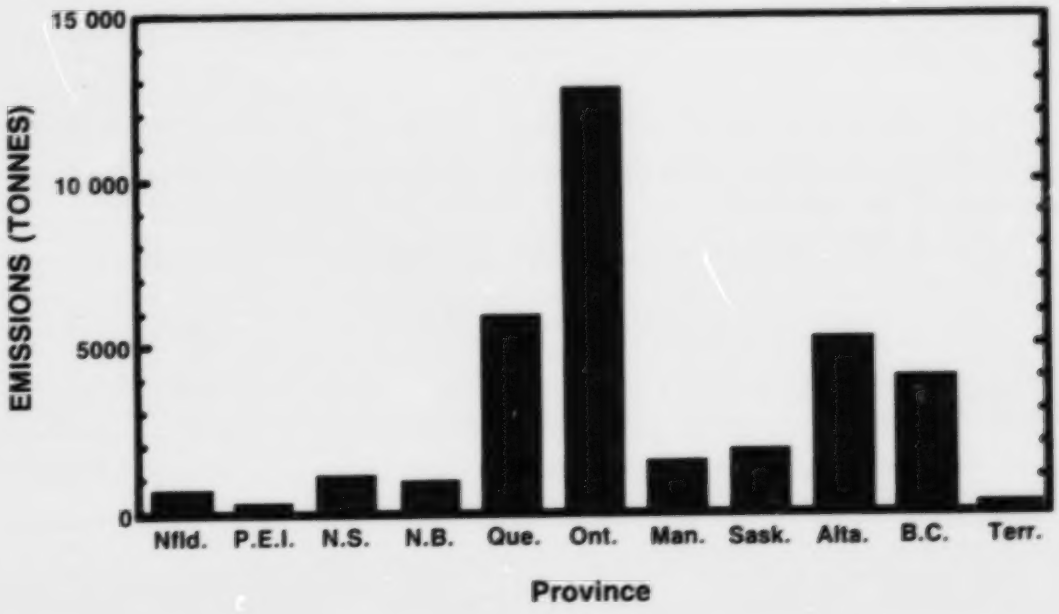

FIGURE S.1 BENZENE EMISSIONS BY PROVINCE

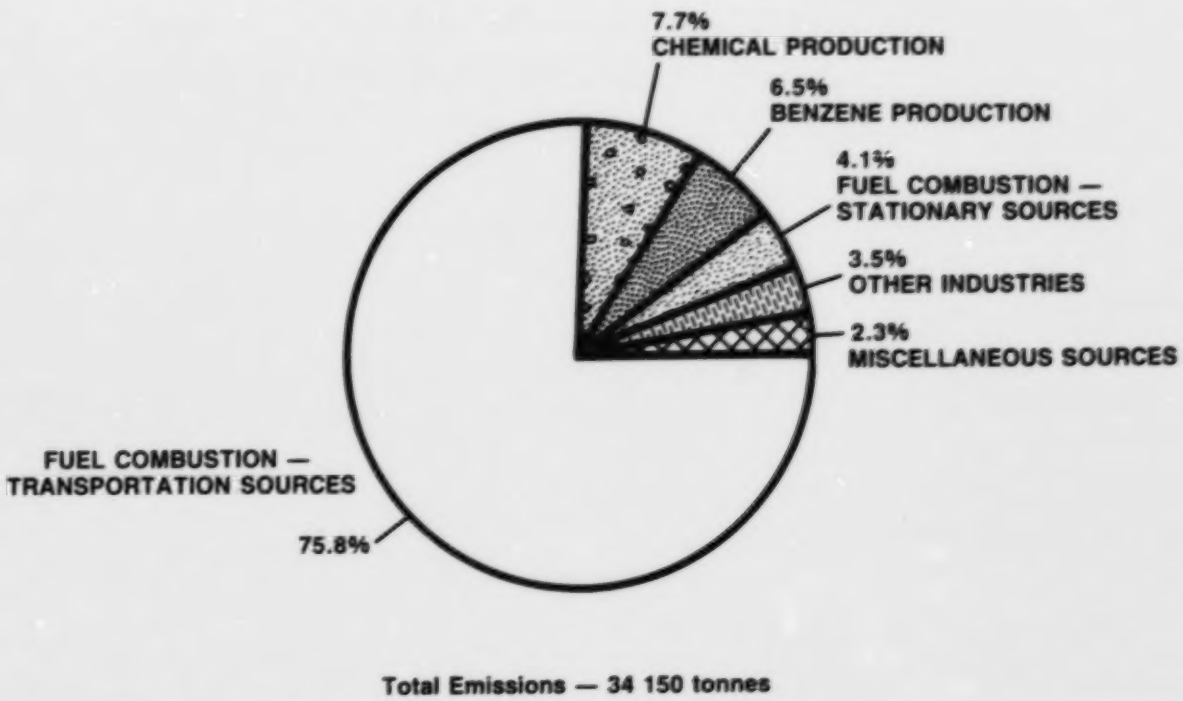

FIGURE S.2 BENZENE EMISSIONS BY SECTOR

1 INTRODUCTION

The purpose of this report is to identify and quantify anthropogenic sources of atmospheric emissions of benzene in Canada for the year 1985. Information presented in this report was obtained from numerous sources, including: published reports, questionnaires, and source test results.

The industrial and chemical processes and activities that generate significant releases of benzene have been described to facilitate the preparation of future emission inventories as well as to provide an understanding of the processes involved.

1.1 Sources and Uses of Benzene

Benzene is a clear, colourless liquid, that is highly inflammable with a low boiling point and high vapour pressure. Soluble with most organic solvents and compounds; benzene is a hexagonal cyclic aromatic hydrocarbon with a ring containing six carbon atoms, with a hydrogen atom attached to each carbon. Benzene is highly refractive, non-polar and nonreactive with low viscosity and low surface tension. Some physical and chemical properties of benzene are listed in Table 1.

Benzene may be produced from petroleum, coal, or natural gas condensates. It exists as a component of gasoline and is used as a solvent and as an intermediate in the

TABLE 1 PHYSICAL PROPERTIES OF BENZENE

Property	Value
Molecular Formula	C_6H_6
Molecular Weight	78.11
Melting Point	5.53°C
Boiling Point (at 101 kPa)	80.1°C
Vapour Density (air = 1)	4.0 at 90°C
Vapour Pressure at 20°C	1 kPa
Flash Point (closed cup)	-11.1°C
Autoignition Point	580°C gasoline 92 octane (390°C)
Surface Tension (at 25°C)	281.8 μN/cm
Specific Gravity (water = 1)	0.879 at 20°C
Heat of Combustion	41.86 kJ/g (constant pressure and 25°C)
Heat of Fusion	9.84 kJ/mole
Heat of Vapourization	33.86 kJ/mole (100°C)
Solubility in Water (% by weight at 20°C)	0.17

production of numerous chemicals including ethylbenzene, cumene, cyclohexane and maleic anhydride.

The low boiling point and high vapour pressure of benzene cause its rapid evaporation at standard pressures and temperatures. Because of its ring structure benzene is basically stable in the atmosphere. It is relatively photochemically inactive and hence, its contributions to photochemistry induced pollutants are minor (1).

Benzene does lend itself to precipitation scavenging, and atmospheric rain washout of benzene to the oceans is a most probable fate. However, benzene rapidly evaporates from water because of its high vapour pressure and poor solubility. This cycle would occur indefinitely were it not for its absorption into and adsorption onto available surfaces (1, 2). Predictive equations, however, show, that virtually all benzene emitted to the environment will reside in the atmosphere (3). The degradation of benzene in the lower atmosphere is photochemically induced indirectly through nitric oxide reactions. It is generally believed that hydroxyl radicals, formed via several intermediate reactions, are the most important reactive species responsible for the breakdown of atmospheric aromatic hydrocarbons and, in particular, benzene (3). The reaction mechanism of benzene with hydroxyl radicals is not completely understood and accurate quantitative predictions of the environmental behaviour of benzene have not been made.

The major sources of man-made environmental pollution from benzene arise from the combustion of gasoline, the production of chemicals using benzene as a feedstock, and refinery operations. Other significant sources include transportation and storage losses from benzene and benzene containing liquids, stationary fuel combustion and coke production.

Benzene is present in fruits, fish, vegetables, nuts, dairy products, beverages and eggs. Concentrations as high as 300 µg/L in water and 2100 µg/kg in eggs have been reported (4).

Measurements of benzene in the ambient air of urban centres have been reported to range from less than 1 to 500 ppb (5). The maximum concentration measured recently in Canada though, is 25 ppb (6). In rural, isolated areas, not significantly influenced by emissions, background levels of about 0.2 ppb are normal (3). Table 2 presents some recent measurements of ambient air concentrations of benzene collected in Canada (6). Although few measurements exist, a comparison with urban levels measured a decade ago, indicates that atmospheric concentrations have decreased significantly and in some cases may now average as little as 20% of earlier values (3, 4).

TABLE 2 SUMMARY OF BENZENE CONCENTRATIONS (ppb) AT CANADIAN MONITORING STATIONS [6]

City	Address	Dates	No. of Samples	Mean	Std. Dev.	Maximum
Sarnia	Centennial Park	Aug.83-Sept.83	8	6.0	4.9	15.3
Toronto	Junction Triangle	Aug.84-Mar.86	105	2.8	1.6	11.6
Montreal	Pointe aux Trembles	Aug.84-Aug.86	83	5.7	4.8	25.1
Vancouver	Rocky Point Park	Dec.85-Jul.86	38	3.2	2.6	11.2
Toronto	26 Breadalbane	Aug.86-Oct.86	13	0.9	0.4	1.6

Note: All data were collected as 24-hour average concentrations.

1.2 Benzene and Human Health

Of the benzene in the environment that enters the body primarily through the lungs, approximately 28 to 50% is rapidly absorbed by the blood [7]. About 50% of the absorbed benzene is eliminated unchanged through the lungs and a small percentage through the kidneys; the remainder is metabolised by the liver enzymes to water soluble derivatives which are excreted in the urine [8]. If benzene levels exceed the capacity of the enzyme system, then benzene accumulates in high fat content areas such as fatty tissue, bone marrow and the brain. Benzene can also be absorbed through ingestion and through the skin.

Estimated annual doses by inhalation vary from 48 mg for an urban dweller to 12 mg for a rural dweller, based on levels in the atmosphere of 4 ppb and 1 ppb, respectively [3]. Annual doses by ingestion, estimated for both food and water are 91 mg for an urban dweller and 0.5 mg for a rural dweller [3]. These estimates are based on an intake of 250 µg/day via food [9] and 1.5 L/day of drinking water with a benzene concentration of 1 ppb.

Acute effects of benzene usually result from inhalation of concentrated benzene vapours in poorly ventilated rooms. A concentration of 20 000 ppm is fatal in 5 to 10 minutes, 7500 ppm is dangerous to life after an exposure time of 30 minutes, 50 to 150 ppm for a period of five hours results in headaches, lassitude and weariness, while a concentration of less than 25 ppm appears to have no short-term effects after an exposure time of eight hours [10]. Since the concentrations at which detrimental effects are

noticed are several orders of magnitude greater than environmental exposure levels, acute toxic effects are not associated with benzene pollution of ambient air. However, for the general public who may be exposed to benzene in the ambient air, albeit at lower concentrations, chronic effects may be important. Long-term exposures to benzene by inhalation in occupational settings have resulted in cytogenetic effects and damage to the blood-forming organ system which includes aplastic anemia and leukemia.

Data on cytogenetic effects of chronic low-level benzene exposure, however, are not conclusive and the relationship between blood abnormalities and chronic exposure is not well established (8, 11). Although the significance of epidemiological data collected on workers exposed to levels of benzene less than 102 ppm is not totally agreed upon, it is widely accepted that individuals exposed to greater levels for at least one to two years have an increased risk of developing leukemia (3). The reader is referred to Health and Welfare Canada's document on benzene (10) and more recent studies, for a detailed discussion on health effects.

1.3 Methodology

Several methods have been used to estimate benzene emissions based on data provided by industry, surveys, and calculations performed by Environment Canada, as well as monitoring data taken from similar processes and emission factors reported in the literature. The emission factor is a statistical average of the rate at which a contaminant is released to the environment, as a result of some activity. It can apply to a part of a process or the whole process; with or without emission controls.

The sources of all emission factors presented in this report have been cited. Most of the emission factors have been developed for materials that contain benzene; therefore, emissions will depend both on the quantity of material processed as well as the concentration of benzene. Benzene is also formed during combustion of certain aromatics; therefore, their content can have a significant effect on estimates. The benzene content of automobile exhaust emissions, for example, increases when the aromatic content is increased, even though the benzene concentration remains the same (12).

In compiling any emission inventory, accurate data on the quantity and characteristics of releases from all sources are required. Although the most accurate means of determining releases is monitoring on a source-by-source basis at the point of release, this is made impractical by the large number and diversity of sources of benzene. Every effort has been made to ensure that the most recent and accurate data available have been used in this report.

2 INDUSTRIAL EMISSIONS

2.1 Crude Oil Operations

Generally, the benzene content of crude oil is low (between 0.15 and 0.2 volume percent) [4]. Nevertheless, emissions can occur from crude oil operations; during production, transportation and storage.

In 1985, Canada produced 63 373 130 m^3 of crude oil [13]. Emissions of benzene from production operations were estimated to be 18 tonnes, based on an emission factor of 0.28 g/m^3 [4,14].

Total crude and equivalents received by Canadian refineries in 1985 were 79 808 060 m^3 [13]. An emission factor of 0.55 g/m^3 was used to calculate emissions from the transportation of crude oil [4,14] which amounted to 44 tonnes in 1985.

Emissions of benzene from storage tanks at refineries were estimated based on the size, type and number of tanks in each province and the most recent storage tank equations for hydrocarbon standing and withdrawal losses [15,16]. A sample calculation along with several emission factors are given in the Appendix. Total emissions of benzene from crude oil storage were estimated at 2 tonnes. Total benzene emissions from crude oil operations were estimated to be 64 tonnes.

2.2 Petroleum Refineries

2.2.1 Refinery Operations. Since crude oil contains small amounts of naturally occurring benzene, some operations at petroleum refineries may emit benzene independent of specific benzene recovery processes. Complete descriptions of the various operations at petroleum refineries is, however, beyond the scope of this report.

Some of the potential sources of benzene emissions in refineries are: process emissions from light and heavy naphtha streams from the crude unit; fluid catalytic cracking units and hydrocracking units; middle distillate storage; lube oil hydrodesulphurization; coking; and heavy hydrocarbon storage and blending [4,17]. Hydrocarbon fugitive emissions also occur from valves, pumps, drains, flanges, relief valves and compressors.

Data do exist on concentrations of benzene in nonmethane hydrocarbon fugitive emissions; however, it was not possible to develop emission factors from these data (Table 3).

Benzene emissions for refinery operations were estimated based on emission factors developed for controlled and uncontrolled sources [4,14]. Although all refineries

TABLE 3 ESTIMATED CONCENTRATIONS OF BENZENE IN NONMETHANE HYDROCARBON FUGITIVE EMISSIONS FOR SELECTED REFINING PROCESSES (17)

Process/Unit	Process Streams (Percent of Total Fugitive Emissions Attributed to Stream)	Benzene Concentration of Stream (ppmw)*
Crude distillation	crude oil (74)	46
	straight run naphtha (24)	59
Aromatics extraction	reformate (12)	648
	aromatic extract (44)	7850
	raffinate (44)	
Delayed coking	cracked naphtha (57)	1642
Fluid catalytic cracking	cracked naphtha (45)	1296
Hydrotreating	straight run naphtha (47)	119
	desulphurized naphtha (47)	119
Catalytic reforming	desulphurized naphtha (47)	119
	reformate (47)	2538
Hydrogen production	straight run naphtha (19)	48

* (ppmw) parts per million, by weight

have some degree of control, it was assumed that those having a capacity less than 5.57×10^3 m^3/day were uncontrolled. The appropriate emission factors used were 6.48 g/m^3 uncontrolled and 1.18 g/m^3 controlled. Based on the number and capacity of each refinery in each province (16), emissions of benzene were estimated at 168 tonnes.

2.2.2 Gasoline Storage. Standing and withdrawal losses of benzene were estimated based on the latest AP-42/API equations for hydrocarbon losses from storage tanks (15,18), the number of tanks, their size, type (floating or fixed roof) and the product stored (16). In addition, a weighted average of 1.81% (vol.) was assumed as the concentration of benzene in gasoline (Table 4). Sample calculations are shown in the Appendix (A.1). Total emissions of benzene in 1985 from gasoline storage were estimated at 134 tonnes.

Total emissions of benzene at petroleum refineries in 1985 were estimated to be 302 tonnes.

TABLE 4 CANADIAN GASOLINE CONSUMPTION AND BENZENE CONCENTRATIONS (1985)

Fuel Blend	Demand (19) ($\times 10^6$ m^3)	Average Benzene Concentration (20) % (vol.)
Leaded	16.50	1.5*
Unleaded	13.42	2.0
Premium unleaded	2.81	2.7
TOTAL	32.73	Weighted Avg. 1.81

* Average of samples was 1.25%; however, 1.5% was used in calculations (see Appendix)

2.3 Benzene Production

Benzene is recovered from petroleum or coal through one of four processes. The greatest amount is derived from petroleum sources through:

1). catalytic reforming of naphtha (and solvent extraction);
2). dealkylation or disproportionation of toluene; or
3). separation of pyrolysis gasoline.

The fourth process is distillation of coke oven light oil. Total production of benzene in 1985 was reported to be 688 000 tonnes (21). The actual production figures of benzene from each of the four processes were not available. Emission sources are identified and available information on emissions of benzene is presented in the following descriptions of the four major production processes. Figure 1 illustrates the various methods used in producing benzene.

2.3.1 Catalytic Reforming/Separation. Catalytic reforming is used to prepare high octane blending stocks for gasoline production and for producing aromatics as separate chemicals. It is associated with the production of toluene and xylene (BTX plants).

Several different solvents may be used to extract or separate benzene (and other aromatics) from the reformate. Glycols (tetraethylene glycol) and sulfolane (1,1 tetrahydrothiophene dioxide) are most commonly used (22,23). The extract is then heated and sent through clay towers to remove any olefins present. Benzene, toluene and xylene are then separated by fractionation.

No source-specific benzene emission factors or estimates were found for catalytic reforming/separation. However, some data indicated that benzene may be

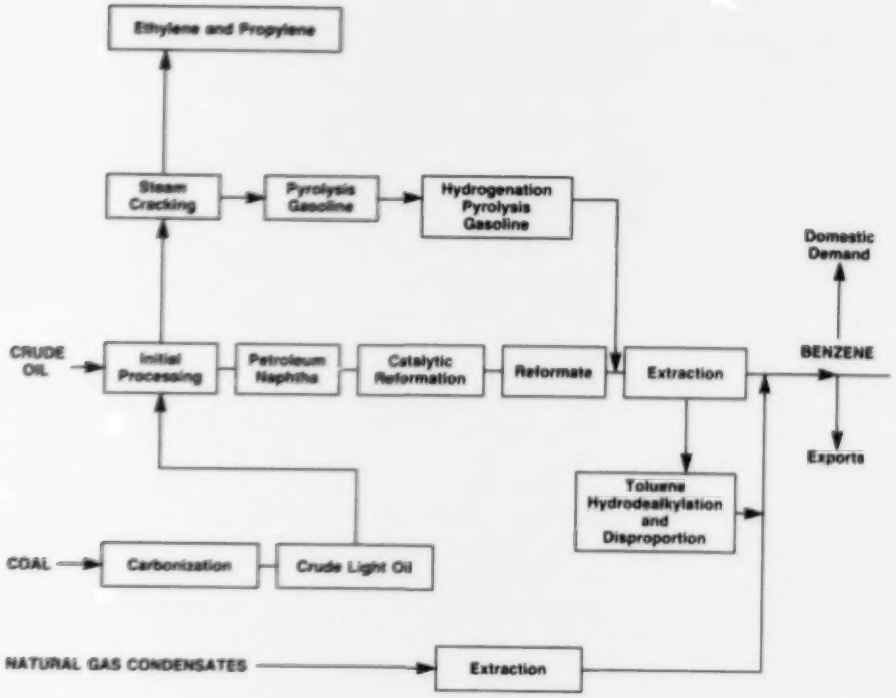

FIGURE 1 BENZENE PRODUCTION IN CANADA

emitted from the catalytic reforming process during catalyst regeneration or replacement, during recycling of hydrogen gas to the reformer and from the light gases taken from the separator (23). One general estimate is that 1% of the total benzene produced by catalytic reforming is emitted (23,24). One description of the Sulfolane process indicated 99.9% recovery or 0.1% emitted (23,24). The unrecovered benzene is not necessarily emitted, but leaves the process in a raffinate stream that may be used as a feedstock.

2.3.2 **Hydrodealkylation.** Benzene may also be produced from toluene through dealkylation or disproportionation. Dealkylation of toluene can be accomplished through thermal or catalytic processes. Pure toluene or toluene mixed with other aromatics or paraffins is heated and is charged to the reactor in the presence of excess hydrogen. Toluene reacts with hydrogen to yield benzene and methane. About 70 to 85% conversion of toluene to benzene is accomplished per pass through the system and the ultimate yield is 95% of theoretical (23).

Toluene disproportionation produces benzene and xylenes by catalytic reaction. The basic process is similar to toluene dealkylation, but can occur under less

severe conditions. No source-specific emission factors were found for benzene emissions from dealkylation or disproportionation of toluene. Potential sources of benzene emissions include the separation of benzene and methane, distillation and catalyst regeneration (24) and in the case of disproportionation, the separation of benzene and xylene and catalyst regeneration.

2.3.3 Pyrolysis Gasoline/Ethylene Production. Ethylene is produced through pyrolysis of natural gas concentrates or petroleum fractions such as naphthas and atmospheric gas oils (25). Pyrolysis gasoline is a liquid by-product formed as part of the steam cracking process and contains a significant amount of benzene, the concentration of which depends on the feedstock. Because the benzene content of pyrolysis gasoline can be high, some plants recover motor gasoline, aromatics (BTX), or benzene from it. In addition, benzene may be emitted from ethylene plants which produce pyrolysis gasoline, but do not recover benzene, although gasoline is a more likely disposition.

The production of ethylene from naphtha/gas oil does not emit large quantities of hydrocarbons or benzenes from process vents during normal operation (25). Emission factors for benzene from sources at ethylene plants are shown in Table 5. The emission factors were developed from data supplied by U.S. ethylene manufacturers (23). Most benzene emissions from ethylene plants are intermittent emissions that occur during plant startup and shutdown, process upsets and emergencies. Fugitive benzene emissions at ethylene plants may originate from pumps, valves, process sampling and continuous process analysis. The emission factor for benzene from storage tanks was derived from AP-42 equations (25). No data were available concerning benzene emissions during recovery of benzene from pyrolysis gasoline. The primary control technique available for intermittent emissions of benzene is flaring.

Based on the emission factors in Table 5 and the quantity of ethylene produced in 1985 (1420 kilotonnes) (26), emissions of benzene from ethylene production were estimated at 172 tonnes.

2.3.4 Coke Oven Light Oil Distillation. Although most benzene is obtained from petroleum, some is recovered through distillation of coke oven light oil. Some coking plants recover light oil, but not all refine it (27). Approximately 11 to 18 L of light oil can be produced from coke ovens producing one tonne of furnace coke. Light oil contains 50% to 85% benzene, 6% to 20% toluene, 1% to 7% xylene, and 0.5% to 4% solvent naphtha (28,29).

TABLE 5 UNCONTROLLED AND CONTROLLED BENZENE EMISSION FACTORS FOR A HYPOTHETICAL ETHYLENE PLANT[25]*

Source	Uncontrolled Emission Factor (g/Mg)**	Controlled Emission Factor (g/Mg)**	Control Option	Efficiency (%)
Compressor Lube Oil Vents				
single compressor train	0.200	-	none	-
dual compressor train	0.400	-	none	-
Other Normal Process Emissions	no significant benzene emissions	-	-	-
Intermittent Emissions		79.2 to 15.8	flares	90 to 98
single compressor train	791.9			
dual compressor train	101.1	10.1 to 2.0		
Storage Tanks	147	22.1	floating roof tank	85
Salt Dome	no benzene emissions			
Fugitives	45.9	8.8	detection/ correction of leaks	80.9
Secondary	21.7	-	none	-

* data are for a hypothetical plant using 50% naphtha/50% gas oil as feed and having an ethylene capacity of 544.2 Gg/yr

** factors expressed as grams of benzene emitted per megagrams of ethylene produced

The coke by-product industry recovers various components of coke oven gas including coal tar, pitch, ammonium sulphate, naphthalene and light oil. Because benzene is contained in the coke oven gas, it may be emitted from coke by-product plants which do not specifically recover or refine benzene. In Canada, four steel mills have coking operations but the extent to which they process coke by-products is not fully known [27]. Emission factors have been developed for coke by-product plants [28] and are shown in Table 6.

TABLE 6 BENZENE EMISSION FACTORS FOR COKE BY-PRODUCT PLANTS (28)

Source	Uncontrolled Emission Factor (g/Mg)	Controlled Emission Factor (g/Mg)	Control Option	Control Efficiency (%)
Cooling Tower				
Direct-water	270	51	- use tar-bottom final cooler	81
		-	- use wash-oil final cooler	100
Tar Bottom	70	-	- use wash-oil final cooler	100
Light-oil Condenser Vent	89	.8	- coke oven gas blanketing from gas holder	98
Naphthalene Separation	87	-		-
Naphthalene Processing	20	-		-
Tar-intercepting Sump	95	1.9	- coke oven gas blanketing from collecting main	98
Tar Dewatering	21	0.42	- coke oven gas blanketing from collecting main	98
		2.1	- wash-oil scrubber	90
Tar Decanter	77	3.9	- coke oven gas blanketing from collecting main	95
Tar Storage	12	0.24	- coke oven gas blanketing from collecting main	98
		1.2	- wash-oil scrubber	90
Light-oil Sump	15	0.3	- source enclosure	98
Light-oil Storage	5.8	0.12	- coke oven gas blanketing from gas holder	98
		0.58	- wash-oil scrubber	90
BTX Storage	5.8	0.12	- coke oven gas blanketing from gas holder	98
		0.58	- wash-oil scrubber	90
Benzene Storage	5.8	0.12	- nitrogen or natural gas blanketing system	98
		0.58	- wash-oil scrubber	90
Flushing-liquor Circulation Tank	9	0.18	- coke oven gas blanketing from collecting main	98
Excess-ammonia Liquor Tank	9	0.18	- coke oven gas blanketing from collecting main	98
			- wash-oil scrubber	90
Wash-oil Decanter	3.8	0.076	- coke oven gas blanketing from gas holder	98
Wash-oil Circulation Tank	3.8	0.076	- coke oven gas blanketing from gas holder	98

Emissions of benzene from the fractionation of light oil have been estimated based on the production of metallurgical coke in 1987 (4600 kt) (30) and an emission factor of 248 g benzene/tonne of coke (29). It should be noted that this emission rate was derived for operations at Dofasco's coke by-product plants from published emission

factors (Table 6) and as such it may not apply to all operations at other plants. Nevertheless, emissions have been estimated on a sector basis and are approximately 1140 tonnes.

2.3.5 Emissions from Benzene Production. As stated, benzene may be emitted from process and storage sources. Process emissions are poorly defined; however, an estimate has been made based on a loss of 0.1% benzene or 0.001 kg benzene/kg benzene produced. This gives total emissions of benzene, from benzene production, of 690 tonnes.

Provincial emissions were estimated by distributing the total by plant production in each province.

Estimates of benzene losses from benzene storage were determined using EPA/API equations as shown in the Appendix (31) and by assuming that 90% of the benzene is stored in fixed-roof tanks, the remaining 10% in floating-roof tanks (4). Total storage emissions were estimated to be 390 tonnes.

Total emissions of benzene from benzene production were estimated to be 2220 tonnes in 1985, of which 51% are attributed to coke oven light oil distillation.

Emissions of benzene from ethylene production were estimated at 172 tonnes in 1985 and are included under chemical production.

2.4 Primary Iron and Steel Production

Iron and steel manufacturing processes include coke production, pig iron manufacture in blast furnaces, steel making using open-hearth, basic oxygen and electric arc furnaces, rolling mill operations, and finishing operations. In 1985, the Canadian steel industry produced approximately 15 million tonnes of crude steel (32).

Organics have been reported in emissions from iron and steel manufacturing sources (33), although no information exists on the benzene content of these emissions. Similarly, emission factors for organics exist for iron foundries and the ferroalloy industry (Table 7).

Potential sources of organics include fuel combustion, the presence of organics on scrap metals and the use of organic binders for pellets and agglomerates. At foundries, organics may be emitted because they are present in core binders and additives, coating oils and paints (34).

Emission factors for benzene from by-product coke production are listed in Table 6. In Canada, metallurgical coke is produced at steel mills and most of the by-product light oil and tars are sold to the chemical industry for further processing (27).

TABLE 7 SUMMARY OF ORGANIC EMISSION FACTORS FOR THE IRON AND STEEL, IRON FOUNDRY, AND FERROALLOY INDUSTRIES [23]

	Normalized Organic Emission Factor (kg/Mg)*
Iron and Steel Industry	
By-product Cokemaking	1.95
Blast Furnace Ironmaking	0.59
Sinter Production	1.6
Basic Oxygen Process Steelmaking	0.0009
Electric Arc Furnace Steelmaking	0.04975
Open Hearth Furnace Steelmaking	0.0094
Hot Forming and Finishing Operations	0.092
Iron Foundry Industry	
Cupola Furnace Melting	0.0975
Electric Arc Furnace Melting	0.08
Inoculation	0.00065
Metal Pouring and Cooling	0.1045
Casting Shakeout	0.945
Ferroalloy Industry	
Open Submerged Arc Furnace Smelting	
Silicon Metal Alloys	5.1
Ferrosilicon Alloys	0.93
Ferromanganese Alloys	0.17
Ferrochromium Alloys	0.3225
Covered Submerged Arc Furnace Smelting	
Ferrosilicon Alloys	0.1125
Ferromanganese Alloys	0.02395
Ferrochromium Alloys	0.0307

* Emission factors normalized to kg/Mg finished product (i.e., total steel products, net castings, total ferroalloys).

Emissions from the basic coke-oven operation can occur from various points during the coking cycle and from the waste-gas stack [34].

Charging can cause varying emissions, depending mainly on the characteristics of the coal and operating practices. Fugitive emissions can result from leaking pipes, apertures, valves and doors.

Benzene emissions from the by-products plant can evolve from the following sources in the light oil handling system: pump seals, condensers, separators, interceptor sumps, storage tank vents and loading facilities as shown in Table 8 (28).

Insufficient data on iron and steel production processes does not permit emissions of benzene to be estimated on a process by process basis. Instead, overall benzene emissions have been estimated based on a general volatile organic compound emission factor of 4 kg/t of coal charged (15), and a benzene to hydrocarbon ratio of 0.0223 in the gas emitted (4). In 1985, approximately 6 500 000 tonnes of coal were consumed in the production of coke, with estimated total emissions of benzene of 343 tonnes.

2.5 Chemical Processes Using Benzene and its Derivatives

Sources of benzene emissions from its use as a feedstock and as a solvent are described in this section. Emission sources are identified, emission factors are presented where available, and emissions quantified. Each process is described briefly and where applicable, emission controls noted.

In 1985, Canadian domestic demand for benzene was 570 kilotonnes (35). Of the total benzene produced, the largest portion was used in the production of ethylbenzene/styrene. Other major chemicals for which benzene was used as a feedstock included cyclohexane, cumene, and maleic anhydride. The demand pattern for benzene in Canada is illustrated in Figure 2.

2.5.1 Ethylbenzene — Styrene. In 1985, production of ethylbenzene amounted to 620 kt, and consumed 445 kt of benzene (35,36). Styrene monomer demand for ethylbenzene was 585 kt (36) and production of styrene amounted to 500 kt (37). The ethylbenzene industry is closely tied to the styrene industry since styrene is produced only from ethylbenzene. There can be approximately a 0.3% by weight carry-over of benzene into ethylbenzene and styrene (38). Additionally, some benzene is reformed in the production of styrene. Ethylbenzene and styrene are produced at three plants in Canada; Polysar and Dow in Sarnia, and Shell in Scotford, Alberta (39).

Process description. Since most ethylbenzene production is integrated with the dehydrogenation process to produce styrene, these processes are described together. The primary reactions are: the catalytic alkylation of benzene with ethylene to produce ethylbenzene; and the catalytic dehydrogenation of ethylbenzene to produce styrene. The process steps are described in the following paragraphs.

TABLE 8 BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT COKE BY-PRODUCT PLANTS [28]

Source	Emission Factors: Uncontrolled (kg/day)		Emission Factors: Controlled (kg/day)		Control Option	Control Efficiency (%)
	Light Oil, BTX Recovery	Light Oil Recovery, Benzene Refining	Light Oil BTX Recovery	Light Oil Recovery, Benzene Refining		
Valves	0.18	0.22	0.07	0.08	- quarterly inspection	63
			0.05	0.06	- monthly inspection	72
			-	-	- use sealed bellows valves	100
Pumps	1.9	2.3	0.5	0.7	- quarterly inspection	71
			0.3	0.4	- monthly inspection	83
			-	-	- use dual mechanical seals	100
Exhausters	0.28	0.28	0.126	0.126	- quarterly inspection	55
			0.10	0.10	- monthly inspection	64
			-	-	- use degassing reservoir vents	100
Pressure Relief Devices	2.7	3.4	1.5	1.9	- quarterly inspection	44
			1.3	1.6	- monthly inspection	52
			-	-	- use rupture disk system	100
Sampling Connection Systems	0.25	0.31	-	-	- closed-purge sampling	100
Open Ended Lines	0.038	0.047	-	-	- plug or cap	100

Note: Factors are based on the total VOC emissions from petroleum refineries and the percent of benzene in light oil and refined benzene [28].

Both fresh feed and recycled benzene are dried to remove water. Dry benzene and ethylene are reacted using aluminum chloride as the catalyst and ethyl chloride as the promoter. The reaction products are cooled, then passed through a settler where the heavy catalyst complex is removed and recycled to the alkylator.

Next, crude ethylbenzene from the settler is washed with water and neutralized with a caustic solution. The crude ethylbenzene contains 40 to 55% benzene, 10 to 20% polyethylbenzene (PEB) and high-boiling point materials. Benzene, ethylbenzene, and polyethylbenzenes are separated in a series of distillation columns.

The purified ethylbenzene is preheated in a heat exchanger. The resultant vapour is then mixed continuously with steam at 710°C in the dehydrogenation reactor, containing a selective catalyst. The reaction products are cooled, condensing the steam, styrene, toluene, and benzene. The condensed mixture is processed through a series of distillation columns to produce styrene, benzene, toluene, ethylbenzene, and tar.

Emission sources and controls. Major process emission sources are: the alkylation reactor area vents, vacuum column vents, and the hydrogen separation vent (40). Other emission sources include storage losses, shipment losses and fugitive emissions from valves and other equipment leaks.

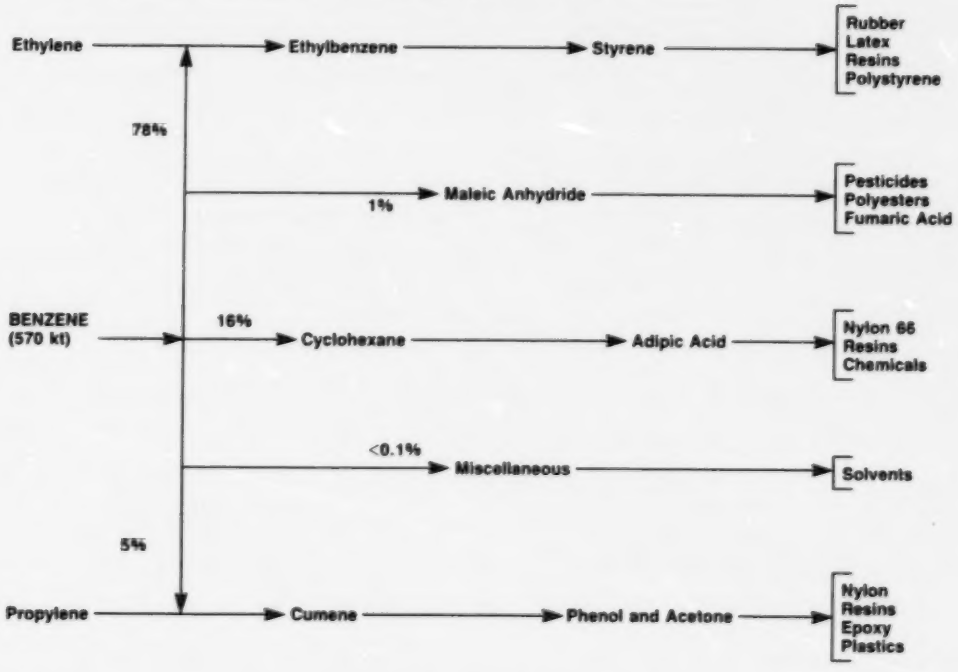

FIGURE 2 DEMAND AND USE OF BENZENE IN CANADA (1985)

Reactor area vents remove various inerts plus entrained aromatics (benzene). Inerts include nitrogen or methane used in pressure control, unreacted ethylene, reaction by-products, and ethylene feed impurities. In typical plants using a liquid phase $AlCl_3$ catalyst with high purity ethylene, vent streams are usually cooled and scrubbed to recover aromatics. Atmospheric and column vents remove non-combustibles in the column feeds, light aliphatic hydrocarbons and any entrained aromatics. Most emissions occur in the first column of the distillation train (benzene recovery column). Vacuum column vents remove air that leaks into the column, light hydrocarbons and hydrogen formed in dehydrogenation, non-combustibles in the column feed and entrained aromatics. Vents can be flared but are only efficient ((99%) emission controls) when flair diameter and gas flow are closely matched for optimum turbulence and mixing. They can be better controlled when the stream is routed to a manifold and burned with other fuels. Benzene in shipping and storage must also be considered as a source where benzene is not produced on-site.

Emissions. Emission factors are based on a 300-kilotonne capacity model plant and are shown in Table 9 (40). Actual emission factors may vary with throughput and control measures and therefore should not be taken as indicative of any particular plant.

Emissions were estimated based on several assumptions. Due to the lack of specific information relating to existing controls, emissions were estimated by taking the average between the estimated uncontrolled and partially controlled emissions. Total emissions from ethylbenzene/styrene production in 1985 were estimated to be 2260 tonnes. Provincial emissions were estimated based on plant capacities.

2.5.2 Cyclohexane. In 1985, production of cyclohexane amounted to 100 kt, with consumption of benzene, 90 kt. However, with the closure of Gulf Canada's Montreal operation at the end of 1985, two of the major end use markets for benzene disappeared; cumene and cyclohexane (41).

Process description. Cyclohexane is produced by the catalytic hydrogenation of benzene. High purity benzene is fed to catalytic reactors in parallel and hydrogen is fed into the reactors in series. This process is carried out in the liquid phase by contacting benzene, hydrogen, and recycled cyclohexane over a nickel catalyst. The cyclohexane leaving the flash separator is sent to a distillation column (stabilizer) for removal of methane, ethane, other light hydrocarbons and soluble gas from the cyclohexane product. Cyclohexane purified in the stabilizer may be greater than 99.9% pure.

TABLE 9 EMISSION FACTORS FOR ETHYLBENZENE/STYRENE PRODUCTION VIA ALKYLATION AND DEHYDROGENATION

Emission Sources	Uncontrolled (g/kg)	Control Device	% Efficiency	Controlled g/kg
Alkylation Reactor Area Vents	0.3	Process heater	99.9+	0.0003
Atmospheric/Pressure Column Vents	1.2	Flare	60 to 99	0.012 to 0.48
Benzene-Toluene Vacuum Vent	3.0	Flare	60 to 99	0.03 to 1.2
Other Vacuum Vents	0.05	Flare	60 to 99	0.0005 to 0.002
Hydrogen Separation Vent	0.003	Flare	60 to 99	0.00003 to 0.0012
Storage and Handling	0.57	Floating roof	85	0.086
		Vented to flare	99	0.00057
		Refrigerated vent condenser	80	0.114
Fugitive	0.11	Detection and correction	74	0.029
Secondary	0.067	None	---	0.067

Note: emission factors are expressed as g benzene emitted per kg ethylbenzene/styrene produced

Emission sources and controls. There are no process emissions during normal operation [42]. During shutdowns, individual equipment vents are opened as required during final depressurization of equipment. Except for the feed streams, the concentration of benzene in the process equipment is low; therefore, little or no benzene emissions are expected during a shutdown.

Fugitive leaks can emit benzene or other hydrocarbons. Fugitive emissions from process pumps, valves and compressors may also contain benzene.

Storage of benzene may also contribute to benzene emissions. Other potential sources of emissions are catalyst handling and absorber wastewater. The controls available for fugitive emissions are an inspection/maintenance program and for storage facilities, the use of internal floating roof tanks.

Emissions. Emission factors have been developed for a hypothetical 150-kilotonne plant and may not apply to any specific plant (Table 10) [23]. Based on production of 100 kilotonnes of cyclohexane and storage of 90 kilotonnes of benzene, emissions for 1985 were estimated to be 47 tonnes.

TABLE 10 EMISSION FACTORS FOR BENZENE FROM CYCLOHEXANE PRODUCTION VIA BENZENE HYDROGENATION

Source	Uncontrolled Emissions (g/Mg)	Controlled Emissions (g/Mg)	Control Technique	Efficiency (%)
Benzene Storage	421	63.2	Internal Floating Roof Tanks	85
Process Fugitives	51.4	11.7	Inspection/Maintenance	80

2.5.3 Cumene. In 1985, production of cumene amounted to 38.5 kt and consumed 26 kt of benzene [35,43]. Production of cumene in Canada ceased after closure of Gulf Canada's Montreal operation in 1985 [43].

Process description. Cumene is produced by alkylating benzene with propylene. Benzene and propylene are reacted at high temperatures and pressures in the presence of an acidic catalyst, usually solid phosphoric acid. Propylene and benzene are introduced into a pressurized combined feed drum and from the feed drum they are sent to the reactor. From the reactor, the by-products, unreacted material and the product are separated by distillation. There are three distillation towers, one each for the rejection of propane unreacted benzene (which is recycled), and the cumene product.

Emission sources and controls. In the solid phosphoric acid process, the cumene column vent is a potential source of benzene. Methane is used to pressurize the system. This methane is eventually vented, carrying with it other hydrocarbon vapours.

Emissions. Emissions were estimated based on a reported benzene concentration in the distillation vent of 38.5% by weight and a total volatile organic emission rate of 0.03 kg/t product [23,33]. Emissions were estimated at less than one tonne for 1985.

2.5.4 Phenol. In 1985, production of phenol amounted to 41 kt [44]. Phenol was produced in two provinces, British Columbia and Quebec.

Process description. Phenol is manufactured in Canada by two different processes: cumene peroxidation and toluene oxidation. The production of phenol via

cumene peroxidation essentially involves two steps. First, air is introduced into an emulsion of purified cumene to produce cumene hydroperoxide. Then, dilute sulphuric acid is added to cleave the compound directly into phenol and acetone. The acetone is separated by distillation and phenol is recovered from the finishing column.

Toluene is converted to phenol in two liquid-phase air oxidation steps: first, toluene is oxidized to benzoic acid and then the benzoic acid is oxidized to phenol. In this process, benzene is present in minute quantities in the toluene feedstock, resulting in process emissions.

Emission sources and controls. Spent air from the oxidizer is the largest source of benzene emissions at cumene-process phenol plants (38). Some emission factors have been reported for some sources which vary from 2×10^{-3}kg benzene/tonne phenol from a post oxidizer concentration condenser vent (23,38) to 15 kg benzene/tonne phenol for plants using the cumene peroxidation method of phenol production.

Emissions. Total emissions of benzene from phenol production have been estimated at 62 t for 1985, based on an emission factor of 1.5×10^{-3} kg benzene/kg phenol.

2.5.5 Maleic Anhydride. In 1985, production of maleic anhydride amounted to 6.1 kt and consumed 8.5 kt of benzene (45).

Process description. Maleic anhydride is produced from the oxidation of benzene in the presence of a suitable catalyst. The reaction is conducted in the vapour phase utilizing a vanadium pentoxide catalyst. Benzene is mixed with an excess of preheated air before being admitted to a reactor. Exhaust vapours, consisting of maleic anhydride, maleic acid, carbon oxides, water and benzene, are cooled and passed through a partial condenser and separator, where the bulk of the maleic anhydride is separated from the noncondensibles. The remaining crude maleic acid is converted to the anhydride and distilled as a final purification step.

Emission sources and controls. The most significant process source of benzene emissions is the product-recovery condenser vent. Scrubbers are usually equipped to recover uncondensed maleic anhydride before venting effluent gases to the atmosphere.

Emissions. Emissions of benzene have been estimated using 1985 Canadian production values and published emission factors (15,33). A hydrocarbon emission factor for maleic anhydride was reported as 87 kg/t. A United States Environmental Protection Agency (U.S. EPA) product profile reported benzene as 16% of the total volatile organic compound (VOC) emissions. Total emissions of benzene were estimated at 85 t. It should be noted that emissions of benzene from maleic anhydride plants are no longer considered

significant in the United States, where maleic anhydride is now produced using butane (23).

2.5.6 Solvent Operations. Although benzene has been used widely as an industrial solvent, increasing awareness of its toxicity has caused many users to replace it with other solvents for most applications. It is not known what industries are still using benzene as a solvent but Table 11 presents industries and manufactured products possibly using benzene.

TABLE 11 INDUSTRIES AND MANUFACTURED PRODUCTS POSSIBLY USING BENZENE AS A SOLVENT

- rubber tires	- floor coverings
- miscellaneous rubber products	- laboratories
- adhesives manufacture	- degreasing of metal furniture, primary metals
- gravure printing inks	- pharmaceuticals manufacture
- printing and publishing	- alcohols production
- trade and industrial paints	- miscellaneous small volume chemicals
- paint removers	- general organic synthesis
- synthetic rubber	- textiles

Note: Many of these industries in the U.S. have reported that benzene is no longer used (23); however, the extent of use in Canada is unknown.

In 1985, miscellaneous demand for benzene was 500 t (35). The major user was the Canadian paints and pigments industry which consumed approximately 5×10^6 L of benzene-containing solvents (i.e., mineral spirits and naphtha, both containing an average of 5% (vol.) benzene). This corresponds to about 250 m^3 of benzene or 220 t. If we assume that all of the miscellaneous demand for benzene is for solvents, and that emissions of nonhalogenated solvents are essentially equal to solvent usage, then a conservative estimate of total emissions from solvent usage is 500 t.

2.6 Asphalt Plants

Hot-mix asphalt is produced by mixing proportioned quantities of aggregates, such as sand, slag or fragments of stone and gravel with hot asphalt.

Emissions of hydrocarbons have been reported from the exhaust gases (4) and emission factors have been developed for some of the processes involved. These include

the rotary dryer, storage piles, and the emissions resulting from the combustion of fuels such as distillate oil and natural gas. One study reported that benzene can be present in the stack gases in quantities less than 3.24×10^{-3} $\mu g/m^3$ [46]. Emissions of benzene have not been estimated, however, because of insufficient data. Any emissions resulting from the burning of fuels at asphalt plants, though, are covered in the Industrial Fuel Combustion section.

3 EMISSIONS FROM FUEL COMBUSTION

3.1 Stationary Sources

Examples of stationary combustion sources are: utility, industrial, commercial and institutional boilers; commercial and domestic combustion units; and process heaters, furnaces, kilns. Coal, oil, and natural gas are the major fossil fuels used by these sources. Stationary sources have been grouped under four categories: power generation by utilities, industrial fuel combustion, commercial fuel combustion, and residential fuel combustion.

Small amounts of hydrocarbons, including benzene, are produced and emitted during coal, oil, gas, and wood combustion. As a rule though, the concentrations of hydrocarbons produced during combustion are very small and only reach significant levels if the unit is operated improperly or not maintained (23). The normal procedure followed in controlling unburned or partially burned hydrocarbons is to increase the combustion efficiency of the unit.

Aromatic components in distillate oils have been reported to be increasing and can range from 5 to 30% and even higher in some cases (8). Only a few measurements have been performed, however, and emission data are rarely representative since a number of factors, such as age and type of burner and boiler, as well as firing parameters in the combustion zone significantly influence emissions. Nevertheless, emissions have been estimated based on available information.

3.1.1 Power Generation by Utilities. In 1985, electricity generated by coal-fired stations accounted for 54.6% of total thermal generation; oil-fired, 4.9%; natural gas, 1.3%; and nuclear, 39.2%. Hydro-powered generation accounted for 67.1% of the total generation of 446 413 GWh (47).

Two basic systems are used to generate thermal power from fossil fuels: steam generation, and internal combustion (gas turbine and reciprocating engines). Steam turbine boilers are fired with coal, heavy fuel oil, crude oil or natural gas (initial steam may be raised by light fuel oil, natural gas, kerosene or diesel oil), whereas reciprocating engines use light oil, natural gas, a combination of both or diesel oil.

Emissions of benzene have been based on the following emission factors: 0.1 mg/kg fuel for coal-fired power plants, and 0.375 mg/kg fuel for oil-fired power plants (48). A natural gas fired furnace had a reported VOC emission factor of 0.018 kg/10^6 m^3 and a benzene concentration of 4% by weight (33). One study reported

exhaust gas emissions of 30 µg benzene/m^3 and 10 µg benzene/m^3 for an oil-fired boiler and a coal-fired boiler, respectively (8).

Based on these emission factors and the quantities of fuels used (39 388 kt of coal, 1 160 000 m^3 of heavy oil, and 590 x 10^6 m^3 of natural gas), emissions of benzene from power generation were estimated at four tonnes for 1985.

3.1.2 Industrial Fuel Combustion. In 1985, approximately 1 676 000 t of coal, 2 994 700 m^3 of heavy oil, 634 000 m^3 of light oil, and 19 x 10^9 m^3 of natural gas were used for industrial purposes (49).

No specific emission test data were found for industrial boilers; however, based on the assumption that emissions are similar to those from utility boilers, emissions of benzene were estimated at one tonne for 1985.

3.1.3 Commercial Fuel Combustion. Approximately 36 000 t of coal, 338 000 m^3 of heavy oil, 1 217 000 m^3 of light oil, and 10 734 400 x 10^3 m^3 of natural gas were used for commercial purposes in 1985 (49).

As with industrial fuel combustion, no specific emission test data were found. Emissions were estimated based on the same emission factors found for utility boilers and were estimated to be less than one tonne for 1985.

3.1.4 Residential Fuel Combustion. In Canada in 1985, approximately 182 000 t of coal, 95 100 m^3 of heavy oil, 4 881 600 m^3 of light oil, 13.33 x 10^9 m^3 of natural gas and 6 244 000 t of wood were used by domestic dwellings (49,50).

Emissions of benzene from coal and natural gas combustion were estimated based on the emission factors given previously. Emissions factors for residential oil combustion were found in the literature and ranged from 0.34 to 29.5 mg/kg (8). According to the National Swedish Environment Protection Board, wood combustion in residential burners can create benzene emissions of 1 to 100 mg/m^3 in the flue gas (8). These concentrations are from 100 to 10 000 times greater than those reported for coal-fired power plants (48). Based on the coal-fired power plant benzene emission factor of 0.1 mg/kg, emission factors have been developed and range from 0.005 to 0.5 g/kg. Other sources reported emissions of benzene from fuel wood combustion of (0.042 to 3.06 g/kg), based on hydrocarbon emission factors of (0.7 to 51 g/kg) and a benzene concentration of 6% (15,18,33).

Emissions of benzene from residential fuel combustion are significant for fuel wood and may range from 300 to 6000 tonnes. Further refinement is not possible with

available data; however, based on engineering judgement, total emissions have been estimated at 1400 tonnes.

A detailed analysis, along with the assumptions made are contained in the Appendix (A.2.1). Emissions have been estimated based on four types of wood stoves commonly used. The emission factors applied for each of these stoves have been derived based on a range of values reported in the literature.

It should be noted that the emissions are only estimates and that further test work is recommended in order to confirm the results.

3.2 Transportation Sources

3.2.1 Gasoline-powered Road Motor Vehicles. Emissions from all gasoline-powered vehicles driven on public roads, including automobiles, trucks, buses and motorcycles are discussed in this section.

Benzene is not added to gasoline but is formed during its manufacture, either during catalytic reforming or steam cracking. Catalytic reforming, the most important process for making high octane number motor gasoline components, produces benzene as part of the reaction to increase the octane number of the naphtha used as feedstock. The production of benzene is unavoidable using current refining technology. The reformate from this process can contain from 1 to 11% (vol.) benzene (51). Benzene also occurs naturally in small quantities in crude oil.

A minor amount of motor gasoline component is obtained as a by-product of the petro-chemical industry. In the steam cracking of the naphtha fraction of crude oil to make ethylene, steam cracker gasoline (or pyrolysis gasoline) is produced which has a high benzene content (20 to 50%) (51,52). These are the main sources of benzene in gasoline and there are many reasons for the wide variations in content, such as:

1) the specifications, particularly octane numbers, of the gasolines and the ratio of premium to regular grades;
2) the crude oil type available;
3) the type of process plant used for gasoline production in the refinery;
4) the proportion of motor gasoline in the total refinery product make;
5) the extracted benzene;
6) the lead alkyl content allowable.

In Canada, the benzene content can range from 0.8% to 5% (vol.) (4).

Emission sources and controls. Hydrocarbons may be emitted from gasoline-powered vehicles from the carburetor (evaporation), fuel tank (vents), crankcase (blow-by past piston rings) and engine exhaust (23). The level of benzene emissions from these sources depends on the gasoline blend. If the fuel contains ethylbenzene, for example, incomplete combustion may lead to conversion of ethylbenzene to benzene (53). Furthermore, there is some evidence that toluene dealkylation occurs, emitting small amounts of benzene (54). Some work indicates that the benzene fraction of exhaust hydrocarbon emissions, increases linearly with increasing benzene content and that increasing the aromatic content of the fuel, while keeping the benzene concentration constant, increases the benzene content of the exhaust hydrocarbons (12). This second result is of particular interest since it suggests that the higher molecular weight aromatics are precursors of benzene. The quantitative influence of these two fuel variables on benzene exhaust emissions appears to be additive (12). It also appears that more than 50% of the benzene emitted from motor vehicles is formed during the combustion of gasoline and is not from the benzene present in the fuel (12,51). The fraction of benzene in the exhaust varies depending on the vehicle type, fuel type, and control technology but is generally between 2% and 5% (12,55). The fraction of benzene in the evaporative emissions also depends on control technology (e.g., whether the vehicle has fuel injection or a carburetor) and fuel composition (e.g., benzene level and Reid vapour pressure) and is generally between 1% and 3%.

Control technologies are available and in use for both evaporative and exhaust emissions of benzene. Positive crankcase ventilation (PCV) and evaporative controls reduce evaporative emissions of benzene. PCV systems circulate air through the crankcase to pick up blow-by gases and take them to the intake manifold where they enter the combustion chamber. An absorption/regeneration system, one of the most common evaporative control techniques, uses a canister of activated carbon to trap vapours and then feeds them back to the combustion chamber.

Emissions. The difference in benzene emissions in vehicle exhaust for vehicles tested under different roadway conditions (urban expressway and stop/go city driving) was considered in several recent studies using the Federal Test Procedure and different control technologies. The results of these studies have been used in estimating emissions and are shown, along with the calculations, in the Appendix.

Benzene emissions in Canada have not been estimated based entirely on U.S. data. Mobile 3C, a computer model of the Canadian fleet was used to derive hydrocarbon emissions, which in turn were used to estimate benzene emissions.

Based on Environment Canada's laboratory analyses of benzene contents in Canadian gasoline, which indicated average benzene levels of 1.5, 2.0 and 2.7% by volume in leaded, unleaded, and premium unleaded gasolines, respectively; benzene to hydrocarbon exhaust and evaporative relationships, an assumption of 25% by volume aromatic content in the gasoline and the mobile 3C computer model; 1985 total emissions of benzene were estimated at 21 916 tonnes. This estimate compares favourably with one made using technology penetration, derived benzene/carbon monoxide relationships and developed predictive equations (6).

3.2.2 Off-road Use of Gasoline. Gasoline consumed in off-road uses is defined as that which is not consumed by road motor vehicles and includes gasoline consumed by construction equipment, agricultural equipment, forestry equipment, and general utility equipment. Approximately 6% of the gasoline sold in Canada was consumed by off-road vehicles.

Gasoline consumption figures were obtained from Statistics Canada and amounted to approximately 2×10^9 L (56).

An average hydrocarbon emission factor of 24.10 kg/m^3 was used (57), along with a benzene to hydrocarbon ratio of 0.035 (55,58). Total emissions of benzene were estimated at 1730 tonnes in 1985.

3.2.3 Aircraft. Two main types of aircraft are considered in this section: reciprocating (piston), and gas turbine. Both types are further divided into subclasses depending on the size of the aircraft and the most commonly used engine for that class. The types of aircraft included in this section are jets, turboprops, piston-engined planes and helicopters.

Although there is a significant amount of data pertaining to emissions of hydrocarbons, only one source was found relating to benzene emissions. Benzene concentrations, as a percentage of hydrocarbon emissions, ranged from 1.93% (weight) for commercial aircraft to 2.93% (weight) for general aircraft (33). Hydrocarbon emissions were calculated based on the U.S. EPA data for inflight and landing cycles (57).

Total hydrocarbon emissions from aircraft amounted to 11 500 t in 1985 (59). Assuming that 2.5% of these emissions were benzene (33), then total emissions of benzene from aircraft in 1985 were estimated to be 288 tonnes.

3.2.4 Rail Transport. Emissions from rail transport are based on the quantities of fuels consumed in the production of energy for locomotion. The only fuel considered is

diesel oil. Emissions have been estimated for 1985 based on a benzene to total hydrocarbon ratio of 0.0073 (60); a hydrocarbon emission factor of 4.9 kg/m^3 (57); and rail diesel oil consumption of 2210 x 10^6 L (49). Total emissions of benzene were estimated to be 80 tonnes.

3.2.5 Marine Transport. The sectors of marine transport considered are ships that use diesel oil and gasoline-powered outboard motors. Emissions were estimated by assuming that the benzene to total hydrocarbon ratio is 0.0073 (similar to that of rail diesel engines) and applying it to the total hydrocarbon emissions. (A sample calculation of which is given in the Appendix, A.2.2). Total emissions of benzene from diesel oil usage were estimated to be 30 tonnes.

For outboard motors, a hydrocarbon emission factor of 115.6 g/kWh was used (57), an average of 6.8 kW and 50 hours of use were assumed and the percentage benzene in the exhaust was assumed to be 2.5%. No test results were found in the literature relating benzene emissions to outboard motors and hence care should be exercised in interpreting the results. Total emissions of benzene from outboard motors were estimated at 670 t for 1985.

3.2.6 Diesel-powered Road Motor Vehicles. Benzene emissions from all diesel-powered vehicles driven on public roads, including automobiles, trucks and buses have been estimated based on hydrocarbon emissions (see Appendix, A.2.2) and a benzene to hydrocarbon ratio of 0.019. Emissions were estimated to be 716 t for 1985 (15,57,58).

3.2.7 Other Diesel-powered Vehicles. Benzene emissions from diesel-powered engines used in the mining, manufacturing, forestry, public administration, construction and agriculture sectors of the economy were estimated using hydrocarbon emission factors from the A.P.-42 publication and applying them in varying percentages, to the vehicles assumed to be used in each sector (see Appendix, A.2.2). Similar to the on-road diesel-sector, a benzene to hydrocarbon ratio of 0.019 was assumed (15,57,58). Based on these factors, total emissions of benzene were calculated to be 465 tonnes.

4 EMISSIONS FROM WASTE INCINERATION

4.1 Municipal Refuse Incineration

Municipal incineration is a process that reduces the volume of solid waste by burning. Some incinerators are best suited for incineration of a waste with particular physical characteristics. Typical municipal refuse incinerators consist of either refractory-lined or water walled combustion chambers with a grate upon which refuse is burned.

Very little information exists on emissions of benzene from incinerators. Benzene has been identified in air emissions from hazardous waste incinerators (61), along with toluene, chloroform, naphthalene and tetrachloroethylene. Several reasons have been offered to explain the prevalence of benzene in the emissions. Due to the low concentration of benzene and the other compounds in the waste feed, the destruction efficiency for the compounds could be poor, the compounds could be input from sources other than the waste feed or the compounds could be actual products of some combustion reactions. No emission factors were given, although the reported benzene content of the stack effluent ranged from 12 to 670 pg/m^3.

One test report of a hospital refuse incinerator showed mass benzene emission rates of 45.5 to 181.8 g/h (23). The dual chamber incinerator had an average feed rate of 356 kg refuse/h during the test. The feed consisted of 10% moisture, 30% plastic, 65% paper and 5% other material. An emission factor of 0.128 g benzene/kg refuse incinerated has been developed based on these data.

In 1985, approximately 909 000 t of refuse were disposed of in Canadian incinerators (62). Total benzene emissions from municipal refuse incineration in 1985 were estimated to be 116 tonnes.*

4.2 Sewage Sludge Incineration

As with municipal refuse incineration, emissions of benzene are a function of the benzene concentration in the sludge and the operating characteristics of the particular furnace. No benzene emission data were found and therefore benzene emissions from sewage sludge incineration have not been estimated for 1985. Approximately 111 000 t of sewage sludge were incinerated in Canada in 1985 (62).

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* The reader is cautioned to exercise care when quoting this result, since neither the operating characteristics nor the feed of any particular incinerator were used in making this estimate.

5 EMISSIONS FROM MISCELLANEOUS SOURCES

5.1 Gasoline Marketing

Gasoline storage and distribution activities represent potential sources of hydrocarbon emissions. Benzene, as a component of gasoline, also has the potential of being emitted. Consequently, total hydrocarbon emissions resulting from storage tanks, material transfer, and vehicle refueling also include emissions of benzene.

A general flow diagram of the gasoline marketing system in Canada is shown in Figure 3 (63). From the refinery, gasoline may be transported by tank truck, rail, pipeline, or ship to intermediate stations known as bulk or marketing terminals, or directly to service stations or commercial users. From the marketing terminals, gasoline is transferred to bulk plants by rail or tank truck. Tank trucks then transfer the gasoline to service stations or commercial users.

Each operation in which gasoline is transferred or stored is a potential source of benzene emissions. At bulk terminals and bulk plants, loading and unloading gasoline and storing gasoline are sources of benzene emissions. Transportation by pipeline is not considered a significant source of emissions.

Gasoline loading into tank trucks is accomplished by essentially two methods: splash loading, or submerged loading. In splash loading, gasoline is introduced into the tank truck directly through a compartment located on top of the truck and as a result, high levels of vapour loss occur. In submerged loading, gasoline is introduced below the liquid surface in the tank, thereby reducing the vapours released.

Storage emissions of benzene at bulk terminals and bulk plants depend on the type of storage tank used. Emissions from marketing tank losses were estimated based on a general hydrocarbon emission factor of 0.34 kg/m^3 (63).

Service station emissions of hydrocarbons are generated when vapours in the underground storage tank are displaced into the atmosphere as the gasoline is being unloaded from the truck. Emissions also occur in underground tank breathing and vehicle refueling operations.

Emissions of benzene were estimated using the hydrocarbon emission factors given in Table 12 by applying a benzene/VOC ratio of 0.006 and by using the gasoline figures given by Statistics Canada (49,57,64). Several assumptions were made in order to compute the provincial emissions. Submerged loading was used for 90% of the deliveries and the splash method for the remainder. Shipping of fuel to central marketing terminals

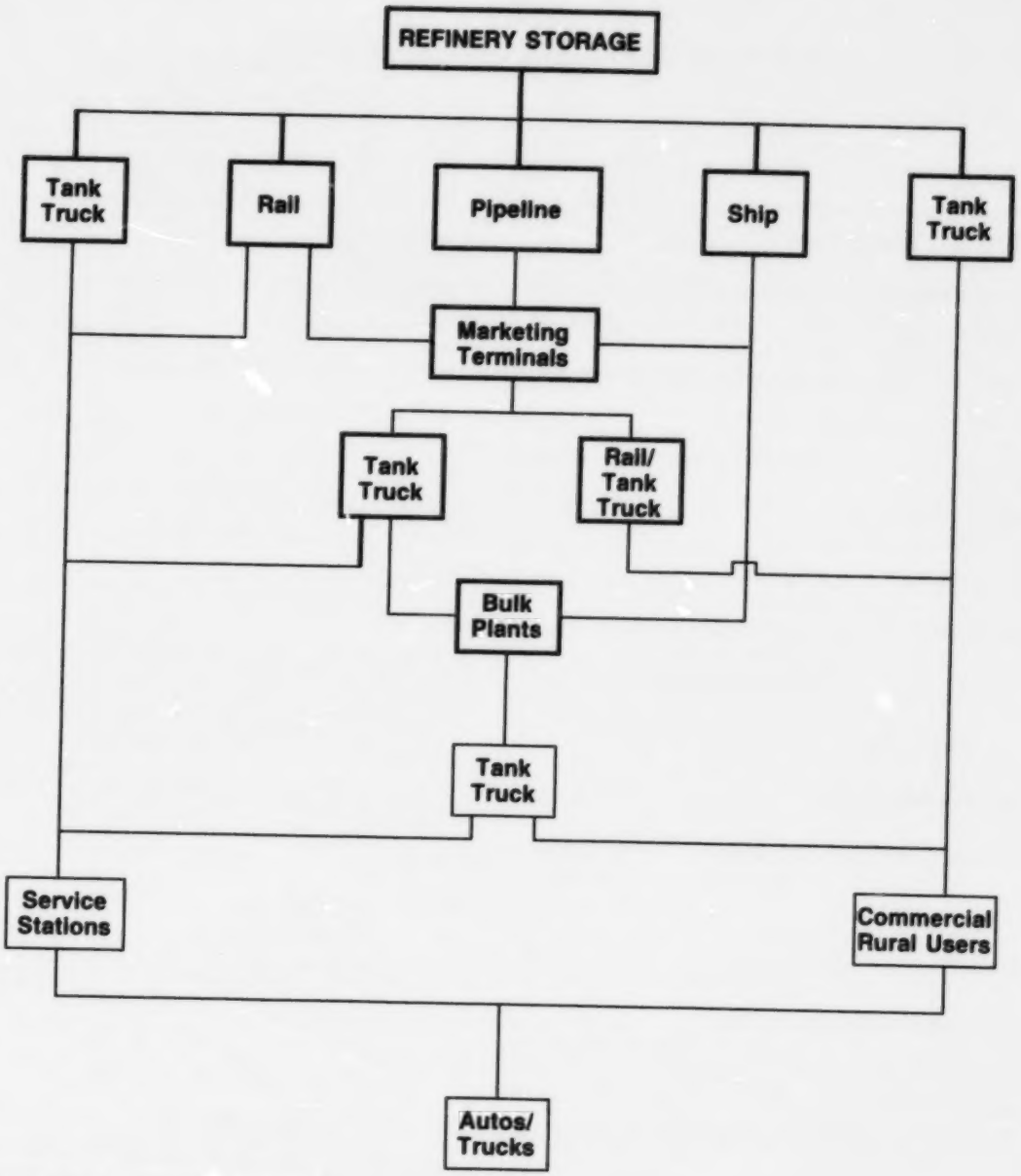

FIGURE 3 GASOLINE MARKETING DISTRIBUTION SYSTEM IN CANADA

TABLE 12 GASOLINE MARKETING EMISSION FACTORS

Source			Emission Factors ($kg/10^3$ L)
Rail and Truck Tanks			
Loading:	Submerged		0.59
	Submerged with vapour balance		0.98
	Splash		1.43
	Splash with vapour balance		0.98
Transit losses:	Loaded (with product)		0 to 0.001
	Unloaded (with vapour)		0 to 0.013
Marine Vessels			
Loading:	Uncleaned tanks		0.315
	Ballasted tanks		0.205
	Cleaned tanks		0.180
	Gas-free tanks		0.085
	Typical Overall*		0.215
Ballasting:			0.100
Transit losses:			0.320
Filling Underground tank:		Submerged	0.880
		Splash	1.380
		Submerged with vapour balance	0.040
Underground tank breathing:			0.120
Vehicle refueling:	Usual		1.375
	With vapour recovery		0.132
	Spillage		0.080

* Assume: 41% uncleaned, 11% ballasted, 24% cleaned, 24% gas-free.

was assumed as: Maritimes 50%, Quebec and Ontario 10%, Prairies 0%, and B.C. 15%. Both loading and unloading operations were accounted for while transit losses of 0.32 kg/m^3 were assumed. Underground tanks at service stations were assumed to be loaded by the submerged method while vehicle refueling was assumed to be by standard methods. Detailed calculations are given in the Appendix (A.3).

Total emissions of benzene for 1985 from gasoline marketing were estimated to be 654 tonnes.

5.2 Benzene Loading and Unloading Operations

Benzene, not transported by pipeline, is transported principally by tank trucks, rail tank cars and ships. As with gasoline, major emissions are assumed to occur during loading and unloading operations. These emissions may be generated by top (splash or submerged) and bottom loading of benzene into transit vehicles or by evaporative loss from spillage due to overfilling of tank cars or accidental discharge of benzene retained in transfer lines. The exact quantities of benzene transported by each of the various methods were not available. In order to estimate emissions, however, several assumptions were made. First, it was assumed that due to the proximity of producers to users, in each of the three producing provinces, all but 10 kt of benzene were transported by pipeline. In addition, it was assumed that all exports of benzene were made either by truck or ship. The total amount of benzene transported was therefore estimated to be 142 kt, (35,36,37), 86% of which was assumed to be shipped and 14% trucked (35). Emission factors of 0.092 kg/m^3 for tank car/truck loading and 0.15 kg/m^3 for marine loading were used to estimate emissions (60,65). Total emissions were estimated to be 25 tonnes.

6 EMISSION TRENDS

Emissions of benzene are greatly influenced by mobile sources, which account for almost 80% of the total. The remaining major sources are the chemical producers and petroleum refiners, which together account for 12% of the total benzene emissions.

Although the demand for benzene as a feedstock increased more than 100% (from 262 kt in 1976 to 570 kt in 1985), emissions have not followed suit. Comparisons with earlier estimates, however, are difficult because of the different methods used in preparing them. Emissions from chemical processes in this report have been estimated based on available test results, whereas the previous inventory relied solely on estimates provided by the chemical industry, the source and derivation of which remain unknown (66). Nevertheless, a clear trend can be seen in emissions of benzene which overall, follows that of gasoline-powered motor vehicles.

Mobile sources currently account for about 50% of the total hydrocarbon emissions; a decrease of 10% from 1970 values. Of this, approximately 80% is contributed by road motor vehicles; 60% of which is due to automobiles.

Historical and future emissions of benzene and a comparison of them with total hydrocarbon emissions are shown in Figure 4.

From 1970 to 1980, emissions of benzene closely paralleled emissions of total hydrocarbons. The increase in emissions during the period 1970 to 1975, was due to the rate of growth in population outstripping the fleet average improvement in emission controls. The population of automobiles and light-duty gasoline trucks grew 34% and 56%, respectively; while the fleet average emission factors decreased only 24% and 19%, respectively. Consequently, hydrocarbon emissions increased about 6%, while benzene emissions increased 4%.

During this period, lower hydrocarbon and therefore benzene emissions were achieved solely by adjusting the carburetion, timing, and by injection of air into the exhaust manifold.

The decreasing trend in both benzene and hydrocarbon emissions began in 1975 and coincided with the introduction of oxidation catalysts. Although only 8% of the 1975 model year vehicles sold in Canada had catalytic converters, their effect over the next few years was to cause a rapid decline in the fleet average emission factors. The decrease in fleet average emission factors for automobiles of 40% and light-duty gasoline trucks of 29%, completely outweighed any population increases and consequently, emissions declined.

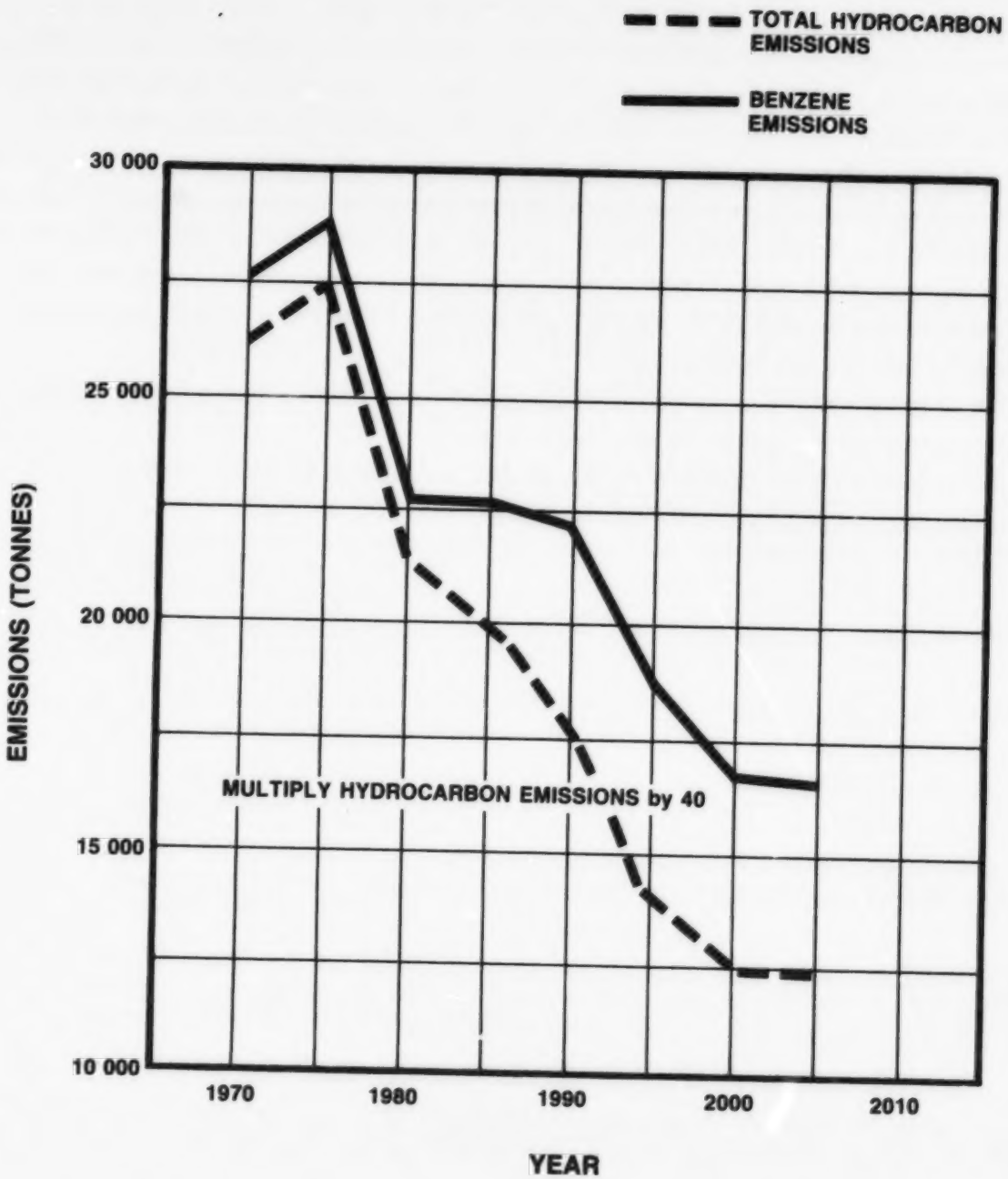

FIGURE 4 EMISSION TRENDS AND PROJECTIONS FOR ROAD MOTOR VEHICLES

Despite a steadily increasing population, both emissions of benzene and total hydrocarbons continued to decline after 1980. However, from 1980 to 1990, benzene emissions no longer mirror hydrocarbon emissions. Two factors contributed to the slower decline in benzene emissions. First, with the increased use and projected increase in use of unleaded gasoline, the pool average benzene content of gasolines rose from approximately 1.8% (vol.) in 1980 to 2.5% (vol.) in 1990. Second, with the increase in use of dual-bed catalysts and three-way oxidation catalysts, great improvements were made in controlling total hydrocarbon emissions. In so doing, however, the benzene fraction of the exhaust emissions rose. These factors, taken together, resulted in a reduction of benzene emissions of only 2% from 1980 to 1990, while emissions of total hydrocarbons declined by 16% over the same period.

After 1990, benzene emissions are projected to follow hydrocarbon emissions, since no significant changes to the fleet are forecast.

Overall, from 1970 to 2005, emissions of benzene and hydrocarbons from road motor vehicles, are projected to decline by 40% and 55%, respectively.

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APPENDIX

SAMPLE EMISSION CALCULATIONS

APPENDIX SAMPLE EMISSION CALCULATIONS

A.1 Storage Tank Emissions. Storage tank emissions were calculated for both fixed-roof and floating-roof tanks. The number, size and type of tanks were derived from a PACE report (16). General emission factors were developed using the assumptions given in Table A-1. For fixed-roof tanks, total evaporative losses amounted to the sum of breathing and working losses.

TABLE A-1 STORAGE TANK CALCULATION ASSUMPTIONS (No Controls)

Ambient Conditions		
Storage Temperature		15.6°C (60°F)
Daily Temperature Change		8.3°C (15°F)
Wind Velocity		4.5 m/s (10 mph)
Tank Dimensions		
67 000 bbl tankage	(10.7×10^6 litres)	
Height		14.6 m (48 ft)
Diameter		33.5 m (110 ft)
250 000 bbl tankage	(39.7×10^6 litres)	
Height		11.4 m (44 ft)
Diameter		60.8 m (200 ft)
Tank Assumptions		
Fixed-roof Tank		
Outage		50 % of tank height
Turnovers annually (N)		13
Paint Factor (F_p)		1.0 (new tank, white paint)
Floating-roof Tank		
Paint Factor (K_p)		0.09 (new tank, white paint)
Seal Factor (K_s)		1.0 (new tank, modern seals)
Tank-type Factor (K_t)		0.045 (new tank, welded)
Seal-related wind speed exponent (n)		1.0
Product Factor (K_c)		1.0
Shell Clingage Factor (C)		0.0015 (light rust)
Number of Columns (N_c)		7 (Note 1)
Effective Column Diameter (F_c)		1.0
Total Deck Fitting Loss Factor (F_f)		750 (Note 2)
Deck Seam Loss (B_d)		0 (welded decks)

Note 1. See Table 4.3-6, AP-42, 4th Edition.
Note 2. See pp. 4.3 21 to 24, AP-42, 4th Edition.

The following equations are applicable to tanks with vertical cylindrical shells and fixed roofs. These tanks must be substantially liquid and vapour tight and must operate approximately at atmospheric pressure.

A.1.1 Fixed Roof - Breathing Loss

$$L_B = 2.26 \times 10^{-2} M_V \left(\frac{P}{P_A - P}\right)^{0.68} D^{1.73} H^{0.51} T^{0.50} F_P C K_C$$

where:

L_B	=	fixed roof breathing loss (lb/yr)
M_V	=	molecular weight of vapour in storage tank (lb/lb mole)
P_A	=	average atmospheric pressure at tank location (psia)
P	=	true vapour pressure at bulk liquid conditions (psia)
D	=	tank diameter (ft)
H	=	average vapour space height, including roof volume correction (ft)
$_T$	=	average ambient diurnal temperature change (°F)
F_P	=	paint factor (dimensionless)
C	=	adjustment factor for small diameter tanks (dimensionless)
K_C	=	product factor (dimensionless). (For crude oil, K_C = .65; for all other organic liquids K_C = 1.0.)

A.1.2 Fixed Roof - Working Loss

$$L_W = 2.4 \times 10^{-5} M_V P V N K_N K_C$$

where:

L_W	=	fixed roof working loss (lb/year)
M_V	=	molecular weight of vapour in storage tank (lb/lb mole)
P	=	true vapour pressure at bulk liquid temperature (psia)
V	=	tank capacity (gal)
N	=	number of turnovers per year (dimensionless)
	N =	$\frac{\text{Total throughput per year (gal)}}{\text{Tank capacity, V (gal)}}$

Total losses from floating-roof tanks are equal to the sum of rim seal, withdrawal, deck fitting and deck seam losses. However, external floating-roof tanks and welded internal floating roofs do not have deck seam losses nor are there any procedures for estimating deck fitting losses. Therefore, emissions have been estimated only for standing (rim seal) and withdrawal losses.

A.1.3 Floating Roof - Standing Losses

$$L_R = K_S V^n P^* D M_V K_C$$

where:

L_R = rim seal loss (lb/year)

K_S = seal factor (lb-mole/(ft (mph)^n yr))

V = average wind speed at tank site (mph)

n = seal related wind speed exponent (dimensionless)

P^* = vapour pressure function (dimensionless)

$$P^* = \frac{\left(\frac{P}{P_A}\right)}{\left[1 + \left(1 - \frac{P}{P_A}\right)^{0.5}\right]^2}$$

where:

P = true vapour pressure at average actual liquid storage temperature (psia)

P_A = average atmospheric pressure at tank location (psia)

D = tank diameter (ft)

M_V = average vapour molecular weight (lb/lb-mole)

K_C = product factor (dimensionless)

A.1.4 Floating Roof - Withdrawal Losses - The withdrawal loss from floating roof storage tanks can be estimated using the following equation.

$$L_W = \left[\frac{(0.943)QCW_L}{D}\right]\left[1 + \left(\frac{N_C F_C}{D}\right)\right]$$

where:

L_W = withdrawal loss (lb/yr)

Q = throughput (bbl/year) (tank capacity (bbl) times annual turnover rate)

C = shell clingage factor (bbl/1000 ft^2)

W_L = average organic liquid density (lb/gal)

D = tank diameter (ft)

N_C = number of columns (dimensionless)

F_C = effective column diameter (ft) (column perimeter (ft)/π)

In order to simplify the calculations, VOC emission factors for fixed-roof and floating-roof tanks were derived and are summarized in Table A-2.

TABLE A-2 PETROLEUM STORAGE VOLATILE ORGANIC COMPOUND EMISSION FACTORS (lb/x 10^3 gal)

	Fixed-roof Tanks			Floating-roof Tanks		
	Breathing Loss		Working Loss	Standing Loss		Withdrawal Loss
Stores Substance	Tank Capacity* (67 000 bbl)	(250 000 bbl)		Tank Capacity* (67 000 bbl)	(250 000 bbl)	
Gasoline						
RVP 13	30.5	22.5	10.0	18.2	8.9	0.0019
RVP 10	23.5	17.4	8.2	13.4	6.5	
Crude Oil						
RVP 5	5.78	4.15	2.47	1.76	0.89	0.007
Naphtha	8.8		6.3	2.50	3.5	1.70

* 1 barrel = 0.159 m^3

Example 1 - Benzene Emissions from the Storage of Crude Oil at B.C. Refineries

Average size of tanks 92.5×10^3 bbl
Number of tanks = 16
100% floating roof
Therefore:

L_S = 1.76 lb / 10^3 gal x (92.5×10^3 x 42) gal x 16
= 109 402 lb
= 50 tonnes

L_W = 0.007 lb / 10^3 gal x (92.5×10^3 x 42) gal x N x 16

N = 12 turnovers
= .007 x 3885 x 12 x 16
= 5221 lb
= 2 tonnes

Total HC emissions = 52 tonnes

Total benzene emissions = 0.002 x 0.4 x 52 tonnes
= 0.04 tonnes

where 0.4 is factor used to convert from liquid-phase concentration to vapour-phase concentration.

Example 2 - Benzene Emissions from the Storage of Gasoline at Saskatchewan Refineries

Fixed-roof Tanks

1 to 12.7×10^3 m^3
10 to 72.1×10^3 m^3
Weighted average 7.71×10^3 m^3

Breathing loss: L_B = 2037×10^3 gal x 30.5 lb/10^3 gal x 11
= 310 tonnes

Working loss: L_W = 2037×10^3 gal x 10 lb/10^3 gal x 11 x 10
= 1321 tonnes

Floating-roof Tanks

three, 44.1×10^3 m^3
Average 14.7×10^3 m^3

Standing loss: L_S = 3883×10^3 gal x 18.2 lb/10^3 gal x 3

= 96 tonnes

Withdrawal loss: L_W = 3883×10^3 gal x .0019 lb/10^3 gal x 3 x 13

= 0.13 tonnes

Total HC losses = 1727 tonnes

Weighted average benzene = 1.81 % (vol.)

Benzene emissions = 1727 x .018 x .4

= 12.4 tonnes

A.2 Emissions from Combustion

Benzene emissions may result from the combustion of gasoline, wood, coal, natural gas, or diesel oil. Some examples are given in the following section.

A.2.1 Emissions from Combustion of Residential Fuel. Table A-3 illustrates the typical composition of Canadian fuel wood.

TABLE A-3 COMPOSITION OF FUEL WOOD

Ultimate Analyses* (%)		Typical Wood (kg/kg wood)
C	49.6 to 53	0.513
H_2	5.8 to 6.7	0.063
O_2	39.8 to 43.8	0.418
S	<1	0.006
N_2	<1	0.006
Ash	<1	0.006
TOTAL		1.00

* Marks Standard Handbook for Mechanical Engineers 5th Edition

Calculation of Wood Combustion Emission Factors

$C + O_2 = CO_2$ (1)

$H_2 + 1/2\ O_2 = H_2O$ (2)

O_2 required for combustion:

$0.513 \times 32/12 = 1.37$ (1)

$0.063 \times 16/2 = 0.50$ (2)

Dry air required for combustion:

O_2 is 0.232 by weight of air

N_2 is 0.768 by weight of air

Equation: 1) becomes $\frac{1.37}{0.232} = 5.91$

2) becomes $\frac{0.50}{0.232} = 2.16$

TOTAL AIR REQUIRED = 8.07 lb/lb fuel

Minus O_2 in the wood:

excess O_2 = 0.418

therefore: excess air = 1.80 at 100% air

Assume 130% air needed for combustion:

$(8.07 - 1.80) \times 1.3 = 8.15$

therefore: excess air = 1.88 lb/lb wood

and excess O_2 = 0.44 lb/lb wood

Products of Combustion:

H_2O ----- $0.063 \times 18/2$ = 0.567

CO_2 ----- $0.513 \times 44/12$ = 1.88

O_2 ----- excess = 0.44

N_2 ----- (0.768×8.15) = 6.26

9.15

That is: 9.15 lb gas/lb dry wood.

Molecular Weight of Air:

23.2% O_2 MW = 32

76.8% N_2 MW = 28

MW air = 32 (0.232) + 28 (0.768) = 28.93

at Normal Temperature and Pressure 1 gram mole occupies 22.4 litres or:

$$1 \text{ mole} = \frac{0.022414}{28.93} \text{ m}^3/\text{g}$$

$$= 7.748 \times 10^{-4} \text{ m}^3/\text{g}$$

For the fuel wood chosen, the volume of flue gas/kg of fuel is:

9.15 kg gas/kg dry wood x 7.748×10^{-1} m^3/kg

= 7.09 m^3/kg wood

Note: This assumes that the wood is dry.

Analysis of Coal Combustion for Comparison Purposes:

Typical Cape Breton Coal Composition:

O_2	7%	
C	78%	calorific value = 32 430 kJ/kg (14 100 Btu/lb)
H_2	5%	
S	2%	
N_2	1%	
Ash	7%	
	100%	

At 130% air for combustion and 149°C stack out temperature, we have 7.65 m^3 of flue gas produced per pound of coal burned or 16.82 m^3 gas/kg coal. This is approximately double that produced for wood.

Using the relationship given in the (OECD) study we can equate volume and weight measurements for both coal and wood, by making certain assumptions.

Benzene emissions from a coal-fired power plant were approximately 10 $\mu g/m^3$ and reported as 0.1 mg/kg coal (Herlan and Mayer, 1980).

Benzene emissions from wood combustion in residential burners range from 1 to 100 mg/m^3 in the flue gas (National Swedish Environment Protection Board, 1981).

Assuming:

1) the combustion of 1 kg of coal produces 16 m^3 of flue gas; and
2) the combustion of 1 kg of wood produces 8 m^3 of flue gas.

If 10 $\mu g/m^3$ of benzene are emitted during coal combustion and this is equivalent to 0.1 mg benzene/kg coal, then (1 to 100 mg/m^3) of benzene we assume can be expressed as (0.005 to 0.5 g benzene/kg) wood.

The U.S. EPA has reported an emission rate for benzene from residential wood combustion of 6%. (This was measured with a catalyst in use.) In addition, AP-42 lists VOC emissions from furnaces of 0.7 g/kg, fireplaces of 13 g/kg and wood stoves of 51 g/kg. These factors imply a range of benzene emission factors of (0.042 to 3.06 g/kg).

In keeping with our hydrocarbon emission methodology for residential wood combustion, however, emissions have been estimated based on four types of fuel wood combustion devices. The fuel usage breakdowns are derived from an Envirobec report "Quantification et prévision des émissions provenant du chauffage résidentiel au bois au Québec" (1983). According to this report, four types of fuelwood combustion devices are widely used. They and their utilization are given as:

Slow Combustion Stove	Conventional Stove*	Fireplace	Furnace
11.8%	24.3%	47.5%	16.4%
VOC E.F.			
51 g/kg	20 g/kg	13 g/kg	0.7 g/kg

* Conventional Stove assumed to be 40% of slow burn.

The fuel wood production was obtained from Statistics Canada - Logging Industry, 25-201 (1984). The total for Canada was 6074 kilotonnes. The benzene emission factors used were derived by arbitrarily choosing estimates within the ranges cited in the literature. In addition, no volatile organic compound emission factor was used that exceeded 16.7 g/kg (i.e., 6% of which equals 1 g benzene/kg wood).

Example 1 - Calculation for Fuel Wood Combustion:

Benzene Emission Factors (kg/tonne)

Furnace	= 0.01	Conventional	= 0.4
Fireplace	= 0.042	Slow	= 1.0

Fuel wood Utilization: (measured in kilotonnes)

	Conventional Stove	Slow Combustion Stove	Fireplace	Furnace
Canada	1476	717	2885	996

Emissions of Benzene = $(0.01\ kg/t \times 996 \times 10^3 t) + (0.042 \times 2885 \times 10^3 t) + (0.4 \times 1476 \times 10^3 t) + (1 \times 717 \times 10^3 t)$

= 1439 tonnes

A.2.2 Emissions from Vehicles

TABLE A-4 BENZENE IN GASOLINE, % (vol./vol.) (summer 1987)(20)

Sample Batch	Company	Location	Gasoline Type		
			Super Unleaded	Unleaded	Regular Leaded
1	Shell	Toronto	4.0	2.0	1.0
2	Petro-Canada	Ottawa	2.7	2.1	1.5
3	Sunoco	Montreal	1.1	1.5	2.3
4	Texaco	Nova Scotia	2.7*	2.7	1.7*
5		Vancouver	1.7 (Chevron)	1.9 (Shell)	0.9 (Esso)

Control Sample:	Expected	Found
Shell unleaded gasoline spiked with 1% benzene	3.0%	2.9%

Note: *Result was confirmed by repeated analysis.

TABLE A-5 EMISSIONS FROM GASOLINE-POWERED ROAD MOTOR VEHICLES

Example ! - Canada (1985)

Vehicle Type	Population	Distance Driven (km)	Hydrocarbon Exhaust (E.F.) (g/km)	Exhaust Emissions (tonnes)	Hydrocarbon Evaporation (E.F.) (g/km)	Evaporation Emissions (tonnes)
Automobiles	11 118 071	15 289	1.93	327 427	1.09	184 838
Light-duty Gasoline Trucks	2 244 085	17 703	3.16	125 399	1.94	77 017
Heavy-duty Gasoline Vehicles	285 646	20 117	2.47	14 211	4.75	27 315
Light-duty Diesel Trucks	201 588	17 703	0.28	998	0	0
Heavy-duty Diesel Vehicles	216 353	82 881	2.04	36 658	0	0
Motorcycles	470 445	2 816	2.27	3 013	1.40	1 852

Benzene Emissions (based on gasoline sales splits and related benzene emission factors).

Gasoline Type (1000 m^3)	Sales Total	Grade Splits (%)	Bz Exhaust E.F. (% HC)	Bz Evap. E.F. (% HC)
Leaded	16 500.1	50	3.1	2.0
Unleaded	13 422.1	41	3.5	2.2
Super unleaded	2 808.3	9	4.0	2.4
Total	32 730.5			

Benzene Emission Calculation - Automobiles - Canada

HC Exhaust Emissions = 327 427 tonnes

HC Evaporative Emissions = 184 838 tonnes

Benzene Emissions (Exhaust)

Leaded gasoline	(327 427 x 0.5) x 0.031	= 5075 tonnes
Unleaded gasoline	(327 427 x 0.41) x 0.035	= 4699 tonnes
Super unleaded gasoline	(327 427 x 0.09) x 0.04	= 1179 tonnes

Benzene Emissions (Evaporative):

Leaded gasoline	(184 838 x 0.5) x 0.02	= 1848 tonnes
Unleaded gasoline	(184 838 x 0.41) x 0.022	= 1667 tonnes
Super unleaded gasoline	(184 838 x 0.09) x 0.024	= 399 tonnes

Total Benzene Emissions from Automobiles ----- 14 867 tonnes

Example 2 - Light-duty Vehicles - Ontario 1985:

Vehicle	Hydrocarbon Exhaust Emissions (tonnes)	Hydrocarbon Evaporative Emissions (tonnes)
Automobiles	120 560	68 058
Light-duty Gasoline Trucks	36 629	22 496
Light-duty Diesel Trucks	291	0
Motorcycles	957	588

Benzene Diesel EF = 0.019 x THC emissions

Gasoline Sales	(x $10m^3$)	(% Total)
Leaded	5 065.3	0.43
Unleaded	5 736.6	0.48
Premium Unleaded	1 034.6	0.09
TOTAL	11 836.5	

	Benzene Exhaust E.F. (% HC)	Benzene Evaporation E.F. (% HC)
Leaded	0.031	0.02
Unleaded	0.035	0.022
Premium	0.04	0.024

	Benzene Emissions (tonnes)		
	Exhaust	Evaporative	Total
Automobiles	4066	1440	5506
Light-duty Gasoline Trucks	1235	476	1711
Light-duty Diesel Trucks	6	0	6
Motorcycles	32	12	44
TOTAL LDV'S Ontario			7267

Mobile 3C was used to generate our hydrocarbon emission factors. Only the percentage benzene of total hydrocarbons was used from Table A-6, in the trends calculations.

TABLE A-6 BENZENE EMISSIONS FOR DIFFERENT EXHAUST EMISSION CONTROL TECHNOLOGIES*

	N	HC (mg/km)	% Benzene	Benzene Emissions (mg/km)
Crowded Urban Expressway				
No Cat/Air	3	0.729	2.42	19.32
Oxid. Cat/No Air	12	0.845	4.11	33.99
Oxid. Cat/Air	10	0.515	3.42	18.64
Dual-Bed Cat/Air	12	0.257	3.83	10.19
3-way Cat/No Air	3	0.099	4.88	5.84
Federal Test Procedures				
No Cat/Air	3	1.388	2.33	32.50
Oxid. Cat/No Air	12	1.218	3.26	38.46
Oxid. Cat/Air	10	1.010	2.81	28.02
Dual-Bed Cat/Air	12	0.375	2.63	10.31
3-way Cat/No Air	3	0.217	4.16	9.13
New York City Cycle				
No Cat/Air	3	4.907	1.81	93.2
Oxid. Cat/No Air	12	3.785	3.03	105.88
Oxid. Cat/Air	10	3.736	2.23	92.15
Dual-Bed Cat/Air	12	1.521	2.14	34.98
3-way Cat/No Air	3	0.864	2.92	25.22

Single-bed; Cat - Catalyst; N - sample size

*Source: Locating and Estimating Air Emissions from Sources of Benzene, U.S. EPA, 450 14-84-007q (1987).

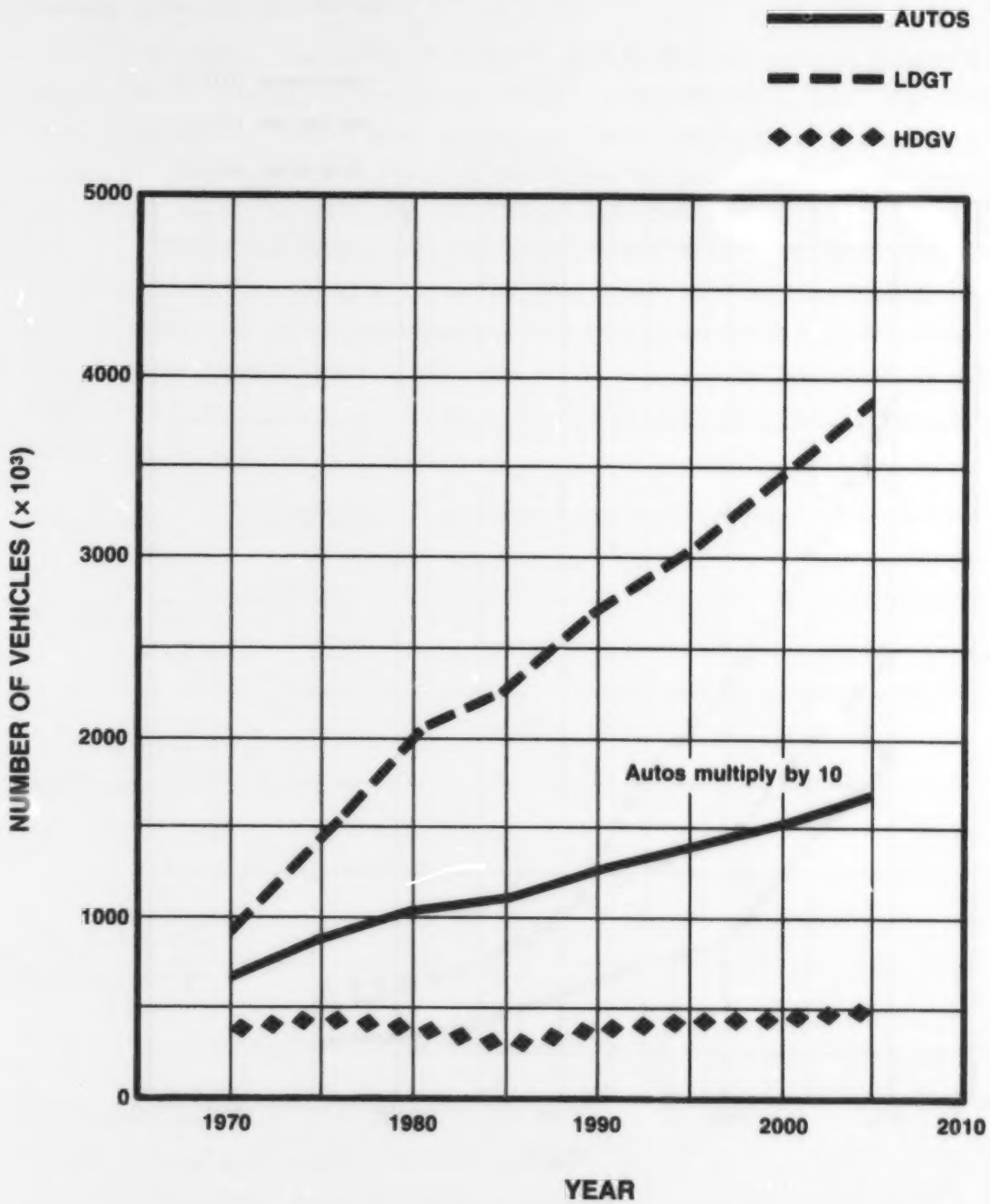

FIGURE A-1 ROAD MOTOR VEHICLES - POPULATION ESTIMATES

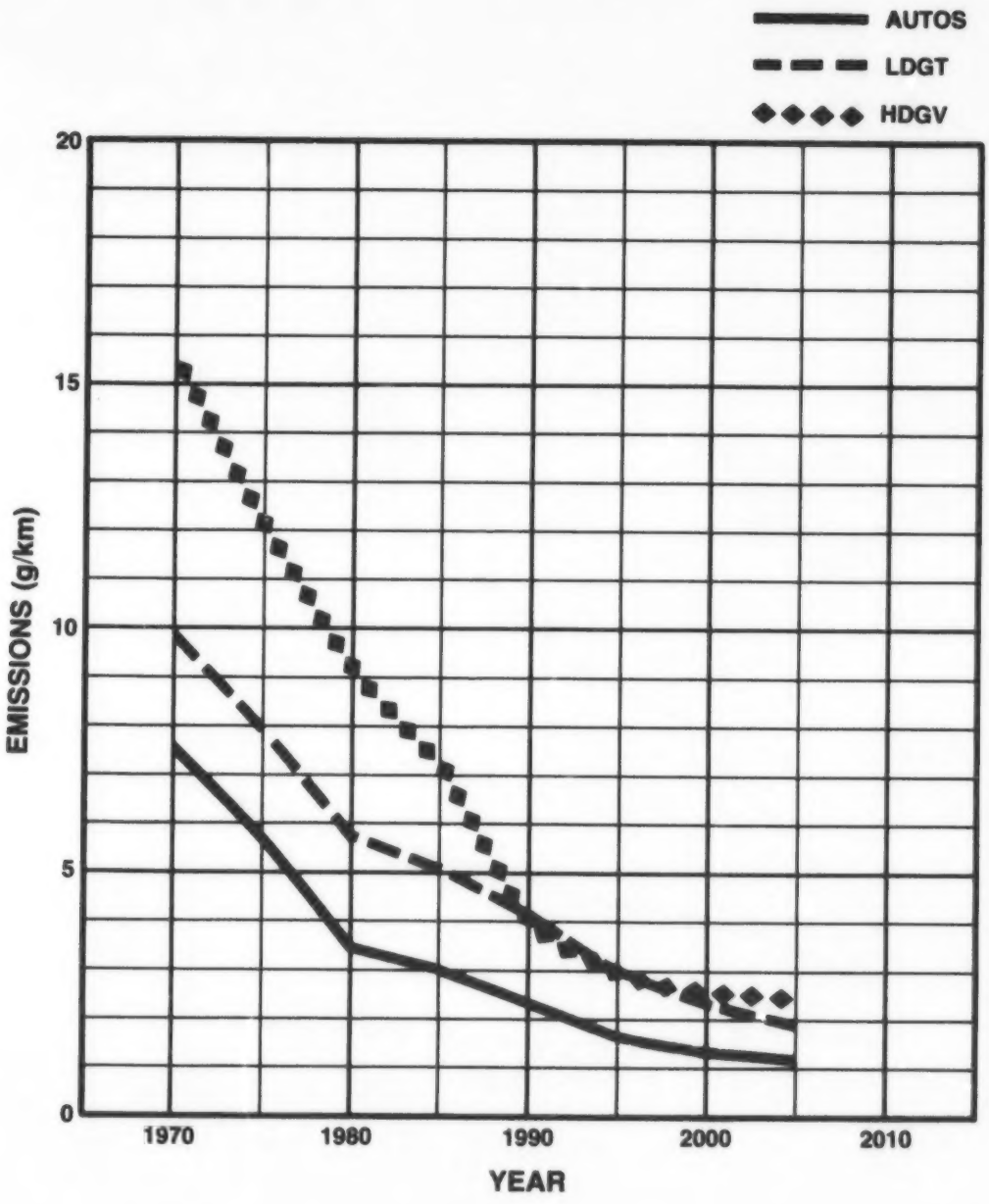

FIGURE A-2 ROAD MOTOR VEHICLES - TOTAL HYDROCARBON EMISSION FACTORS

Transportation Sources - Marine

Emissions were estimated based on two sources where pollutants can be emitted; while underway and while generating auxiliary power in port. For underway motion, Ontario and Quebec were the only provinces considered to produce significant emissions. The quantities of heavy oil and diesel oil used for steam and motor ships respectively, were provided by Statistics Canada, publication (57-003).

The number of calls in port, for steam and motor ships, were obtained on a percentage basis from the total number of calls in port obtained from Statistics Canada Publication (54-210). These percentages were derived by averaging the fractions of steam ships to motor ships reported in 1980 and 1981. Statistics on the number of outboard motors were found in Statistics Canada publication (64-202). An average of 6.8 kW and 50 hours of use per year were assumed.

TABLE A-7 HYDROCARBON EMISSION FACTORS FOR SHIPS

Dockside			
Motor Ships (Diesel oil)		39.8	kg/call in port
Steam Ships (Heavy Oil)		10.9	kg/call in port
Underway			
Motor Ships (Diesel Oil)	Ontario	7.0	g/L
	Quebec	6.0	g/L
Steam Ships (Heavy Oil)		0.08	g/L
Outboard Motors (gasoline)		115.6	g/kWh

Marine Emissions - Hydrocarbon Emissions

Canada	Total ships in port	2069	tonnes
	Total ships underway	1938	tonnes
	Total	4007	tonnes

Benzene Emissions 0.007 3 x 4007 = 29 tonnes

Outboard Motors

Canada Total = 26 688 tonnes

Assuming Benzene emissions to be 2.5%

Benzene emissions = 26 688 x .025 = 667 tonnes

Diesel-powered Road Motor Vehicles

Emissions were calculated in a similar manner to those of gasoline-powered road motor vehicles, excluding evaporative emissions. To the hydrocarbon emissions, a factor of 0.019 was applied to estimate benzene emissions.

Heavy-duty Diesel Trucks

Hydrocarbon emissions --- 36 658 tonnes

Benzene emissions --- 36 658 x 0.019 = 697 tonnes

TABLE A-8 HYDROCARBON EMISSION FACTORS FOR DIESEL-POWERED VEHICLES

Sector	Emission Factors (kg/m^3)
Mining	3.55
Manufacturing	4.49
Forestry	4.45
Public Administration	3.37
Pipelines	4.49
Construction	3.79
Agriculture	7.24

Example Calculation:

Mining - - - - - - - - - - - $938 \times 10^3\ m^3 \times 3.55\ kg/m^3$ = 3329 tonnes

Benzene Emissions - - - - 0.019 x 3329 = 63 tonnes

A.3 Emissions from Gasoline Marketing

Example Calculation - British Columbia

Total gasoline: $3491.3 \times 10^3\ m^3$

Refinery Storage Transfer to Marketing and Bulk Tanks

Truck E.F. —— 0.674 kg/m^3

Ship E.F. —— 0.75 kg/m^3

85% by truck and 15% by ship $\Longrightarrow$ overall E.F. = 0.685 kg/m^3

Marketing tank losses 0.34 kg/m^3

Filling underground tank - - - - - 0.930 kg/m^3

Underground tank breathing- - - 0.12 kg/m^3

Vehicle refuelling - - - - - - - - - 1.375 kg/m^3

Spillage - - - - - - - - - - - - - - - 0.080 kg/m^3

Hydrocarbon Emissions (3491.3×10^3) (0.685 + 0.34 + 0.93 + 0.12 + 1.375 + 0.08)

= 12 324 tonnes

Benzene Emissions = 0.006 x 12324 = 74 tonnes